

# **Combined hydrogen sulfide and carbon dioxide removal process for biogas upgrading**

**Dissertation**

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## Abstract

Biogas upgrading is an efficient method to increase biogas energy value and to offset world energy demand. However, most of the technologies developed today suffer a setback due to high cost, high energy requirement and greenhouse gas emissions due to methane losses. The combined hydrogen sulfide and carbon dioxide removal process, which integrates both biological aerobic desulphurization and bottom ash CO<sub>2</sub> capture method, is a promising alternative for such problems. In the present study, the combined removal process was proved to be technically feasible as well as environmentally safe and economically profitable.

Lab scale and pilot test study of the combined H<sub>2</sub>S and CO<sub>2</sub> removal process proved to enrich methane content of the biogas stream by efficiently removing H<sub>2</sub>S using sulfide-oxidizing bacteria. CO<sub>2</sub> was captured and stored mineralogical by bottom ash.

Individual biotrickling filter designed for H<sub>2</sub>S removal showed removal efficiency of 99 % when the loading rate of H<sub>2</sub>S was 14.2 g S-H<sub>2</sub>S m<sup>-3</sup>·h<sup>-1</sup>. Removal efficiency increased for increasing loading rate until the critical loading point. The FISH analysis confirmed the diverse population of sulfide-oxidizing bacteria in the biotrickling filter. Bottom ash with moisture content was able to absorb CO<sub>2</sub> gas and efficiently converting it into mineral carbonates. The sorption capacity of bottom ash was found to be 14.5 g CO<sub>2</sub>.kg<sup>-1</sup>. The combined removal performance of both process where executed both in lab scale and in the pilot test study. Experimental trials with real biogas proved that the method is technically viable while achieving methane content of 91.1 vol % at the outlet. Life cycle analysis of the combined removal process showed that the global warming potential in terms of kg CO<sub>2</sub>-Eq is least as compared to Pressure swing adsorption method.

Furthermore, a techno-economic analysis was performed to study the economic feasibility and to analyze the hotspots and bottleneck in implementing this technology as compared to that of combined heat and power (CHP) and Pressure swing adsorption (PSA) method.

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## Table of Contents

	Page
Acknowledgment	i
Abstract	ii
Table of Contents	I
List of Abbreviations & Indices	V
List of Figures	IX
List of Tables	X1V
List of Equation	XVI
<b>1 Introduction</b>	<b>1</b>
1.1 Problem, motivation, and objectives	3
<b>2 Biogas and various forms of utilization</b>	<b>4</b>
2.1 Biogas utilization Pathways	4
2.1.1 Biogas use in heat supply	5
2.1.2 Biogas use in CHP	5
2.1.3 Biomethane from biogas	6
2.1.4 Biomethane in the natural gas grid	7
2.2 Biogas upgrading technologies	14
2.3 CO <sub>2</sub> removal techniques	14
2.3.1 Pressure swing adsorption (PSA)	14
2.3.2 Pressure water scrubbing	15
2.3.3 Chemical Scrubbing	18
2.3.4 Membrane Technology	18
2.3.5 Cryogenic separation	18
2.3.6 CO <sub>2</sub> capture and carbon capture and storage (CCS) techniques	21
2.4 CO <sub>2</sub> capture using Bottom ash	22
2.4.1 Origin of bottom ash	22
2.4.2 Physical and chemical properties	22
2.4.3 CO <sub>2</sub> absorption with bottom ash	24

---

---

2.5	H <sub>2</sub> S toxicity and its removal techniques in biogas	26
2.5.1	Physio-chemical methods for H <sub>2</sub> S removal	27
2.5.2	Biological H <sub>2</sub> S removal	28
2.5.3	Sulfide oxidizing bacteria (SOB) and its application in H <sub>2</sub> S degradation	30
2.5.4	Biotrickling filter and recent advances	32
<b>3</b>	<b>Biological aerobic desulphurization for the removal of hydrogen sulfide in biogas</b>	<b>34</b>
3.1	Material and method	34
3.1.1	Biological aerobic desulphurization	34
3.1.2	Design of biological trickling filter	34
3.2	Analytical methods	42
3.2.1	Gas Sampling	42
3.2.2	Liquid Sampling	44
3.2.3	Microorganism source and biomass immobilization	45
3.2.4	Fluorescent in situ hybridization (FISH)	46
3.2.5	Biotrickling filter performance calculations	47
3.3	Results and discussion	49
3.3.1	Startup operation and performance of H <sub>2</sub> S bio trickling filter	49
3.3.2	Inoculum and startup	50
3.3.3	Experimental conditions	50
3.3.4	Effect of loading rate and empty bed residence time (EBRT) on H <sub>2</sub> S removal	51
3.3.5	Effect of Dissolved Oxygen (DO) and sulfate production	53
3.3.6	Elimination capacity (EC) vs. loading rate (LR)	57
3.3.7	Microbiological FISH analysis	59
<b>4</b>	<b>Carbon dioxide capture from biogas using carbonation of bottom ash</b>	<b>61</b>
4.1	Material and method	61
4.1.1	Design of carbonation reactor	61
4.1.2	Experimental conditions	63
4.1.3	Bottom ash collection	63
4.2	Analytical Methods	66

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4.2.1	Gas Analysis	66
4.2.2	Solid Analysis	67
4.2.3	Sorption capacity measurement	67
4.3	Results and Discussion	68
4.3.1	Effect of moisture content	69
4.3.2	Upgrading capacity	71
<b>5</b>	<b>Lab-scale and pilot test study for combined H<sub>2</sub>S and CO<sub>2</sub> removal process for biogas upgrading</b>	<b>74</b>
5.1	Lab scale material and methods	74
5.2	Pilot-scale material and methods	76
5.3	Analytical Methods	79
5.4	Hypothetical explosion risk calculation for biogas during operation of test experiment at Metabolon site, Am Berkebach 1 51789 Lindlar	82
5.5	Results	84
5.5.1	Experimental result from lab scale	84
5.5.2	Experimental results from Metabolon landfill site	85
<b>6</b>	<b>Life cycle Assessment (LCA) and Techno-Economic Analysis for the combined removal process for biogas upgrading</b>	<b>90</b>
6.1	Introduction to Lifecycle Assessment (LCA)	90
6.1.1	Goal and scope definition	91
6.1.2	Inventory Analysis and Assumptions	91
6.2	Techno-Economic Analysis	93
6.2.1	Technical characteristics and support schemes for three scenarios	94
6.3	Results	95
6.3.1	Mass and Energy flow consumptions	95
6.3.2	Environmental impact and process contribution	96
6.3.3	Comparison of LCA for combined removal process and Pressure swing adsorption (PSA) and aerobic desulphurization	99
6.3.4	Global warming potential and Carbon balance	99
<b>7</b>	<b>Conclusion and Outlook</b>	<b>109</b>
7.1	Conclusion	109
7.2	Outlook	112

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## List of Abbreviations & Indices

$\mu$	growth rate
[vol%]	Volume percent
€	Euro
A	half the saturation constant or H <sub>2</sub> S loading rate at 0.5 EC <sub>max</sub> .
ADP E	abiotic depletion elements, abiotic depletion elements
ADP F	abiotic depletion fossil, abiotic depletion fossil
AP	acidification potential, acidification potential
APC	air pollution control
AS	chemical scrubbing using amine
AVEA	Aufbereitungs- und Deponierungsgesellschaft
BA	Bottom ash
BABIU	Bottom Ash for Biogas Upgrading
BAV	Bergisch Waste Management Association
BTF	Biotrickling filter, <i>See</i>
CaCO <sub>3</sub>	calcite
CCS	Carbon Capture and Storage
C <sub>g</sub>	gas phase concentration, gas phase concentration
CH <sub>4</sub>	Methane
CHP	co-generation units for heat and power
C <sub>i</sub>	Liquid phase concentration, Liquid phase concentration
C <sub>in</sub>	pollutant inlet concentration
CML	Centrum voor Milieukunde Leiden
CO <sub>2</sub>	Carbon dioxide
C <sub>out</sub>	Pollutant outlet concentration
CR	Carbonation reactor
CRP	Combined removal process

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CRP BA – AD	combined removal process using bottom ash and aerobic desulphurization
$C_s$	Concentration of substrate dissolved in liquid
CS	cryogenic separation
DG CLIMA	Directorate-General for Climate Action
DM	Dry Matter
DMEA	di-methyl ethanol amine
DO	dissolved oxygen
DVGW G260	Standard for gas injection in public grids, Germany
EBA	European Biogas Association
EBRT	Empty bed residence time
EC	Elimination capacity
$EC_{max}$	maximum elimination capacity in the biotrickling filter
EEG	Renewable energy act
EnWG	German energy industry act
EP	Eutrophication potential, Eutrophication potential
EPRI	Electric power research institute
$E_{sys\ consumed}$	total amount of energy consumed for biogas upgrading process
<i>EU</i>	1, European Union
FAETP	freshwater aquatic ecotoxicity, freshwater aquatic ecotoxicity
FISH	Fluorescence In Situ Hybridization Technique
FQD	Fuel Quality Directive
GasNZV	Ordinance on Gas Network Access
GHG)	greenhouse gas
GWP	global warming potential, global warming potential
h	Moisture content
H	high value gas, <i>See</i>
H <sub>2</sub> S	hydrogen sulphide
HPWS	High pressure water scrubbing

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HRT	hydraulic retention time
IEA	International Energy Agency
ISO	by International standards organization
ISWA	International solid waste association
$K_H$	dimensionless Henry constant
KW	Kilo Watt
KWh	Kilo Watt hour
L	low value gas
L/S	liquid/solid ratio
LBG	Liquid biomethane
LCA	Life cycle analysis
LCI	Life cycle inventory
LEL	Lower explosion limit
LHV	Lower heating value
LR	Loading rate
$L_s$	inlet H <sub>2</sub> S inlet loading rate
m	maintenance energy consumption
$m_{\text{biogas}}$	mass flow rate of raw biogas
MAETP	marine aquatic ecotoxicity potential, marine aquatic ecotoxicity potential
$MCO_2$	molar weight of CO <sub>2</sub>
MEA	mono-ethanol amine
mi	Initial mass of sample
$MJ/m^3$	MegaJoule per cubic meter
MSW	municipal solid waste
MW	Mega Watt
oMSW	organic fraction of municipal solid waste
OPS	Organic physical scrubbing
POCP	photochemical oxidation potential, photochemical oxidation potential
$ppm_v$	Parts per million

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PSA	Pressure Swing Adsorption
PSA - AD	PSA upgrading with aerobic desulphurization
PSD	particle size distribution, <i>See</i>
$Q_{\text{air in}}$	air flow rate
$Q_{\text{biogas}}$	Biogas flow rate
RE	Removal efficiency
RED	Renewable Energy Directive
RT/P	Gas constant
$S^{\circ}$	elemental sulphur
SOB	Sulphur oxidizing bacteria
TAETP	terrestrial ecotoxicity, terrestrial ecotoxicity
UEL	Upper explosion limit
V	Reactor bed volume, Reactor bed volume
$V_{\text{CO}_2}$	Volume of absorbed CO <sub>2</sub>
VSS	volatile suspended solids
WS	wet substance
X	Dry cell weight of biomass in biofilm
$Y_{\text{xs}}$	Yield of dry cell weight
$\eta$	Plant energy efficiency

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## List of Figures

		Page
Figure 2.1	Various forms of Biogas utilization pathways. Biogas upgrading to natural gas quality is the scope of this study.	4
Figure 2.2:	The proportion of biogas utilization showing major use in electricity generation followed by biogas upgrading, adopted from Swedish energy agency	7
Figure 2.3:	Flow pathway of upgraded biogas into the natural gas grid	8
Figure 2.4:	Distribution of carbon emission from biomass to energy generation. (ZEP, 2012)	21
Figure 2.5:	Typical distribution of minerals in bottom ash particle, adopted from (Tang <i>et al.</i> , 2015)	25
Figure 2.6:	Biological sulfur oxidation cycle in H <sub>2</sub> S degradation (Carrera <i>et al.</i> , 2016)	31
Figure 3.1:	Biotrickling filter designed and constructed at University Duisburg Essen. From left: Picture 1 shows the constructed biotrickling filter with the liquid reservoir. Picture 2 shows the column for gas flow (Rajavelu 2015).	36
Figure 3.2:	Typical plastic saddle rings used as a packing material to fill the column of biotrickling filter (Rajavelu 2015).	37
Figure 3.3:	Image of the engineering design constructed at lab scale for the biotrickling filter operation for H <sub>2</sub> S removal.(Rajavelu 2016).	38
Figure 3.4:	layout of the engineering design constructed for biotrickling filter operation. Equipments in the image numbered is explained in table 3.	39
Figure 3.5:	Technical layout of sensors used for gas analysis for H <sub>2</sub> S removal	42
Figure 3.6:	Diagram describing the passage of gas flow from the biotrickling filter to the gas sensors for analysis	43

Figure 3.7:	Variations in Removal efficiency (RE), dissolved oxygen and pH as compared to Empty bed residence time (EBRT). EBRT with 250s showing maximum Removal efficiency of 99%. pH remained the same (1.5) with negligible fluctuations. Each EBRT was maintained for 1.5h.	53
Figure 3.8:	Effect of Empty bed residence time (EBRT)s on sulfate production. Sulfate production increased in recirculation liquid with decreasing the EBRT. Dissolved oxygen showed major fluctuations with increasing sulfate production	56
Figure 3.9:	Effect of Loading rate (LR) versus Elimination capacity (EC) and Removal efficiency (RE) in biotrickling filter. Removal efficiency increased for increasing Loading rate. Elimination capacity decreased after reaching the critical loading rate.	57
Figure 3.10:	Fluorescence pictures of bacteria from biotrickling filter. A) and B) DAPI stained cells and THIO 1 labeled cells from the inoculum sample before acclimatizing in biotrickling filter, Bar 10 $\mu\text{m}$ C) D) and G) samples from biotrickling filter after acclimatization with $\text{H}_2\text{S}$ . Samples were hybridized cells with THIO probe, bar 5 $\mu\text{m}$ ; H) Hybridized cells with ALF 98 probe specific for <i>Acidiphilium</i> spp, Bar 10 $\mu\text{m}$ .	60
Figure 4.1:	Process layout for experimental design on bottom ash $\text{CO}_2$ removal. The gas from gas cylinder passes through the bottom ash reactor where $\text{CO}_2$ is adsorbed. The exit gas is using gas analyzer.	62
Figure 4.2:	Image of bottom ash collection from AVEA GmbH, Leverkusen, Germany (Rajavelu 2016).	65
Figure 4.3:	Image From AVEA GmbH, Germany. Pictures are showing the municipal waste handling as well as incineration inside the furnace. (Rajavelu 2016).	66
Figure 4.4:	Graph showing S-shaped curve obtained with $\text{CO}_2$ gas composition (vol%) versus breakthrough time. The breakthrough time was observed at less than 40 mins after passing of the gas.	69
Figure 4.5:	Graph with breakthrough curve obtained for different Liquid/solid (L/S) ratio (0.05, 0.1, 0.2) for bottom ash samples. Samples with an optimum moisture content of 0.1 took longer time to attain breakthrough point whereas	

---

	samples with higher moisture content (0.2) obtained quicker breakthrough time.	70
Figure 4.6:	Bottom ash samples before and after carbonation.(Rajavelu 2016).	72
Figure 4.7:	Graph with sorption capacity ( $\text{CO}_2$ g/Wet BA (kg)) versus Time (mins). Bottom as samples with Liquid/Solid (L/S) ratio 0.1 showed higher sorption capacity. All samples tested had a size fraction of 0 – 2mm.	73
Figure 5.1:	Experimental Layout for Combined $\text{H}_2\text{S}$ and $\text{CO}_2$ removal process at Labscale. The process and the numbering on equipments are described in the section 5.1	74
Figure 5.2:	Image of the experimental labscale set up for combined removal process designed and installed at University Duisburg Essen (Rajavelu 2016).	75
Figure 5.3:	Image of the experimental set up for the combined $\text{H}_2\text{S}$ and $\text{CO}_2$ removal process installed at Leppe Landfill site: Metabolon, Cologne, Germany (Rajavelu 2016).	78
Figure 5.4:	Location of Leppe landfill site: Metabolon, Cologne Germany. Picture at the left shows landscape view of landfill site; Picture at the right shows the biogas collection point from where sample biogas is drawn off for experimental purpose (Rajavelu 2016).	79
Figure 5.5:	Modified ET -8D gas analyzer system for pilot test study conducted at Metabolon, Germany. Sensors for biogas containing $\text{CH}_4$ , $\text{CO}_2$ , $\text{O}_2$ , $\text{H}_2\text{S}$ (0-100 ppm),(0 -3,000 ppm) are connected to the ET-8D controller from where the measurements are recorded continuously in the computer using RS 232 modibus	80
Figure 5.6:	Graph showing percentage of $\text{H}_2\text{S}$ and $\text{CO}_2$ versus time (mins) at labscale study. $\text{H}_2\text{S}$ concentration remained well below 2 ppm for longer time. $\text{CO}_2$ concentration started to increase few mins thus showing the breakthrough curve	84
Figure 5.7:	Variations in the biogas concentration as a function of time (mins). The $\text{CH}_4$ concentration in biogas started to increase as soon as the gas flow is initiated. $\text{CO}_2$ concentration remained zero (vol%) until the breakthrough point is reached. $\text{O}_2$ remained zero throughout the process. $\text{H}_2\text{S}$	

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	concentration in biogas remained below 20 ppm before passing into bottom ash reactor. The H <sub>2</sub> S concentration in biogas after passing into bottom ash reactor remained below 5 ppm.	87
Figure 5.8:	Experimental result from test M9 showing difference in H <sub>2</sub> S concentration before and after passing onto the bottom ash reactor. There is a clear evidence that H <sub>2</sub> S concentration at the outlet remained well below <4 ppmv after passing through bottom ash indicating that bottom ash adsorption of H <sub>2</sub> S has taken place.	88
Figure 6.1:	Four major steps of Life cycle assessment and the interrelation.	90
Figure 6.2:	Process layout coupling aerobic desulphurisation with bottom ash CO <sub>2</sub> capture for LCA study	92
Figure 6.3:	Life cycle assessment (LCA) for combined removal process method for biogas upgrading. Simplified LCA showing environmental impact for the studied categories	97
Figure 6.4:	Global warming potential (kg CO <sub>2</sub> – Eq) for the production of 1 KWh biomethane from combined removal process	100
Figure 6.5:	Comparison of Life cycle assessment (LCA) for combined removal process and Pressure swing adsorption method (PSA). PSA had higher impact in all categories due to high energy consumption and methane losses	101
Figure 6.6:	Carbon (CO <sub>2</sub> ) balance for the combined removal process layout with inputs from LCA. Inputs include electricity consumption for the whole process, diesel input for transport and input of raw materials.	102
Figure 6.7:	Comparison of operational expenditure (OPEX) for Pressure swing adsorption (PSA) and combined removal process.	105
Figure 6.8:	Economic comparison of three scenarios; Biogas with CHP, Pressure swing adsorption with aerobic desulphurisation (PSA – AD) and Combined removal process with aerobic desulphurisation (CRP –AD)	106

---

<b>List of Tables</b>	<b>Page</b>
Table 2-1: Standards of biomethane quality injection into the natural gas grid. Comparison of requirements from different countries (Allegue and Hinge, 2012)	9
Table 2-2: European countries with national regulations on biomethane from biogas (Allegue and Hinge, 2012)	12
Table 2-3: Comparison of different commercial upgrading technologies (Allegue and Hinge, 2012)	16
Table 2-4: Advantages and disadvantages of diverse commercial upgrading technologies (Allegue and Hinge, 2012)	19
Table 2-5: Maximum leaching of inorganic compounds for building materials (Tang, 2012)	23
Table 2-6: Physical and chemical properties of hydrogen sulfide	26
Table 2-7: Sulphur oxidizing bacteria and their energy sources	28
Table 3-1: Design of trickle bed reactor according to guideline VDI 3478 part 2	35
Table 3-2: Characteristics of plastic rings used for H <sub>2</sub> S removal in biotrickling filter	36
Table 3-3: Composition of nutrient solution used for the growth of Sulfur oxidizing bacteria in biotrickling filter	37
Table 3-4: Technical specifications of bio trickling filter system. Descriptions of components found in figure 3.4.	40
Table 3-5: Technical specification H <sub>2</sub> S sensor	43
Table 3-6: FISH probes used in experiment	47
Table 3-7: Experimental conditions at the startup phase	51
Table 3-8: Experimental conditions with Removal efficiency for each Empty bed residence time (EBRT)	52
Table 3-9: Experimental conditions with variations in sulfate production for each loading rate	55
Table 4-1: Technical details on bottom ash production from AVEA Leverkusen Incineration plant	64

---

Table 4-2	Experimental trials for bottom ash carbonation by gaseous CO <sub>2</sub>	68
Table 4-3:	Mass balance and CO <sub>2</sub> uptake for experimental test trails 1, 2 and 3	72
Table 5-1:	Parameters and operating values for lab scale combined removal process	76
Table 5-2:	Sampling point and sampling measurements for pilot test study	81
Table 5-3:	Typical biogas concentration from the digesters operated at Metabolon landfill site	82
Table 5-4	Results from experimental trials conducted at metabolon landfill sites	89
Table 6-1:	Comparison of energy efficiency for combined removal process and PSA in biogas upgrading.	96
Table 6-2:	Life cycle inventory for the production of 1 kWh of biomethane using combined removal process	98
Table 6-3:	Techno-economic analysis data for three Scenarios	107

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**List of Equations**

2.1	$CO_2 + H_2O \longrightarrow H_2CO_3$ $H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$	25
2.2	$HS^- + \frac{1}{2} O_2 \rightarrow S^0 + OH^-$ $HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	32
3.1	$HS^- + \frac{1}{2} O_2 \rightarrow S^0 + OH^-$ $HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	47
3.2	$LR = [(Q_{\text{biogas}} + Q_{\text{Air IN}} * C_{\text{IN}}) / V$	48
3.3	$RE = [(C_{\text{in}} - C_{\text{out}})] * 100$	48
3.4	$EC = [(Q_{\text{biogas}} + Q_{\text{Air IN}}) * ((C_{\text{in}} - C_{\text{out}}))] / V$	49
3.5	$K_H = C_g / C_i$	52
3.6	$dc/dt = [(\mu/y_{xs}) + m] X$	55
3.7	$EC = EC_{\text{max}} * L_s / L_s + A$	58
4.1	$VCO_2 = \left(\frac{RT}{P}\right) \times \frac{\Delta m}{MCO_2} / (100 - h)m_i$	67
4.2	$Ca(OH)_{2(aq)} + CO_{2(aq)} \rightarrow CaCO_{3(s)} + H_2O_{(liq)}$	71
6.1	$\dot{\eta} = E_{\text{sys produced}} / m_i * LHV_i + E_{\text{sys consumed}}$	95

## 1 Introduction

Biogas production and upgrading have gained worldwide attention due to its enormous potential in meeting energy demand. It has proven to be viable and emerged as a promising technology. Biogas is composed of methane (55 - 75%) and carbon dioxide (30 - 45%) and other impurities such as oxygen (0 - 3%), nitrogen (0 - 15%), ammonia (0 - 100 ppm) and hydrogen sulphide (0 - 10,000 ppm) (Awe *et al.* 2017). Biogas upgrading by definition is the removal of carbon dioxide from biogas to produce a gas with high methane content (greater than 96 %). This gas is called biomethane and is suitable for energy purposes such as use in heat and power production or as a vehicle fuel. Biogas upgrading has gained attention in bioenergy supply chain due to its enormous energy production capacity. Countries like European Union (EU) have already generated 347 PJ in 2009 with more than 6,000 biogas plants (Baciacchi *et al.* 2013)

Many technologies for biogas upgrading are already established and have gained popularity worldwide. They include Pressure Swing Adsorption (PSA), High-pressure water scrubbing (HPWS), chemical scrubbing such as amine scrubbing (AS), membrane separation (MS), organic physical scrubbing (OPS) and cryogenic separation (CS) (Starr *et al.* 2014). According to International Energy Agency bioenergy task 37 (IEA, 2015), there were 220 operating plants for biogas upgrading at the end of 2012. Most of them are in Germany (96), and Sweden (55) and this number is increasing drastically. PSA still has a market share of 40 %, water scrubbing 23 %, and amine scrubbing 22 %. All the technologies mentioned above can obtain biomethane close to 99 %. While technically achievable at all scales, these upgrading technologies suffer a setback in small-scale industries due to high cost and high energy consumption (Bauer *et al.*, 2013). In Europe, a high percentage of the total biogas production comes from many small-scale digesters (50 - 200 m<sup>3</sup> hour<sup>-1</sup>) producing small quantities of biogas (Warren, 2012). Persson, Jonsson, and Wellinger, (2007) identified that the upgrading cost for small-scale plants (<100 m<sup>3</sup> hour<sup>-1</sup>) is around 0.03 - 0.04 € kWh<sup>-1</sup>, and for large plants (200 - 300 m<sup>3</sup> hour<sup>-1</sup>), it is 0.01 - 0.16 € kWh<sup>-1</sup>. Thus smaller plants had a higher cost compared to larger plants

In recent years, Carbon Capture and Storage (CCS) technology (IEA, 2012) has gained attention in EU energy policy and biogas upgrading. The carbon capture and storage by certain minerals such as bottom ash, basic regenerative residues and calcium oxides from cement wastes makes it carbon negative rather than releasing it into the atmosphere which can be carbon neutral. Carbon mineralization is described as a process in which oxides of calcium and other chemical compounds are used as adsorbents for carbon dioxide CO<sub>2</sub> capture from gases such as biogas (MacDowell *et al.* 2010). This process has attracted the researchers in the field of biogas upgrading. Arickx (2010) suggested that municipal solid waste residues such as bottom ash and fly ash are used as a standard absorbent for CO<sub>2</sub> capture from biogas. This process

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popularly termed as BABIU (Bottom Ash for Biogas Upgrading) have been extensively studied both in the laboratory and in pilot scale (Mostbauer *et al.* 2014). The chemical reaction is occurring between the hydroxides present in bottom ash and the CO<sub>2</sub> results in CO<sub>2</sub> capture leading to the conversion of mineral calcium carbonate which can be sold as cement additives or for building purposes. The economic profitability of this technology is already mentioned by Lombardi and Carnevale, (2013). Starr *et al.* (2012) showed that the environmental impact of BABIU process was the lowest compared to five other upgrading technologies. It is also important to mention that BABIU process showed high carbon savings particularly in the presence of less bottom ash transport distances (Pertl, Mostbauer, and Obersteiner, 2010)

With significant improvement in biogas upgrading the attempt to eliminate the toxic hydrogen sulfide H<sub>2</sub>S in raw biogas is still under review due to its corrosive nature. Almost all upgrading units currently developed by companies supply additional H<sub>2</sub>S removal unit for this purpose. Though various H<sub>2</sub>S removal techniques such as physical (Belmabkhout, De Weireld, and Sayari, 2009) and chemical (Peiffer and Gade, 2007) are available, biological H<sub>2</sub>S removal is more favorable and widely accepted in the global market. Its significant low running cost and environmental friendly operational method have attracted numerous patents by various leading companies such as for as DMT sulfuric, THIOPAQ O&G. Studies reveal that aerobic biotrickling filter could perform high H<sub>2</sub>S elimination (280 g S m<sup>-3</sup>h<sup>-1</sup>) under extreme conditions. They employ various microorganisms of species *Thiobacillus* genus (Macalady, Jones and Lyon, 2007) that effectively degrade H<sub>2</sub>S to elemental sulfur and sulfate. The decrease of H<sub>2</sub>S concentration in the gas stream is usually at sufficient speed, particularly in seconds. Sublette and Sylvester, (1987) showed that pure culture of *Thiobacillus spp.* could degrade H<sub>2</sub>S within 1-2 s.

However, aerobic biotrickling filtration has suffered many criticisms due to the need for an additional supply of oxygen in the upgrading unit, which is dangerous as well as it causes biogas dilution to occur. Albeit, concerning the climate change category (kg CO<sub>2</sub> - Eq), aerobic desulphurization emits only 5.24 kg CO<sub>2</sub> per hour while activated carbon desulphurization would emit 15.75 CO<sub>2</sub> per hour per 100 m<sup>3</sup> of biogas cleaned. Nevertheless, the overall environmental impact of biological techniques are much more favorable compared to other chemical and physicochemical techniques (Aroca *et al.* 2007)

Thus, this study aims to combine aerobic desulphurization method with bottom ash CO<sub>2</sub> capture method. This study involves developing an individual aerobic biotrickling filter for H<sub>2</sub>S removal and a CO<sub>2</sub> removal using bottom ash. The two reactors are combined in serial connection and operated. The study includes the technical, environmental and economic feasibility of the system in detail as well as the removal efficiency of two contaminants such as H<sub>2</sub>S and CO<sub>2</sub> is tested.

## 1.1 Problem, motivation, and objectives

In contrast to high energy production, biogas upgrading suffers issues such as high energy requirement, cost, high carbon emissions, and methane losses. It alarms the biogas industry due to the amendments to the EU directives which directs to reduce CO<sub>2</sub> emissions from renewable biofuels. Climate change and carbon emissions are evident globally. Hence the greenhouse gas emission (GHG) savings imposed by the EU directives for biogas utilization is of worth to mention. The two primary directives, Renewable Energy Directive (RED) (20(9/28/E) and Fuel Quality Directive (FQD) (2009/30/E), define a minimum set of CO<sub>2</sub> emissions allowed as a part of sustainability criteria for biofuels. Thus, from January 2018, the GHG emissions have to be reduced by 50 % given the risk of climate change. This concern the biogas upgrading industry in particular as they represent the second most significant carbon emissions in the whole biogas production supply chain. With subsidy end for bioenergy in 2020, it is quintessential for any upgrading technology to prove with high carbon savings. Thus, the primary aim of this thesis is to develop a new biogas upgrading technology by combining two environmentally favorable technologies for H<sub>2</sub>S and CO<sub>2</sub> removal from biogas. Furthermore, technical as well as the environmental feasibility of this new upgrading process is compared with a current market available technology such as Pressure swing adsorption for better understanding. Thus the objectives of the present study can be summarized as follows

- To develop individual lab scale process for hydrogen sulfide removal using aerobic desulphurization method
  - To develop individual lab scale process for carbon dioxide removal from biogas using bottom ash CO<sub>2</sub> capture method
  - To test and optimize both the processes, integrate and evaluate the combined performance
  - To demonstrate the technical feasibility of the combined hydrogen sulfide and carbon dioxide removal process for biogas upgrading at a real scale pilot test method
  - To prove the environmental and economic feasibility of the combined removal process using Life cycle assessment (LCA) method and to compare it with the market available Pressure swing adsorption (PSA) method for biogas upgrading.
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## 2 Biogas and various forms of utilization

### 2.1 Biogas utilization Pathways

European member states have committed to the use of bioenergy supply chain and are ambitious in meeting the renewable energy directive targets. In 2013, 26 % of EU electricity was generated using renewables. Bioenergy generated 500 TWh of electricity in the year 2011 accounted for 2 % world electricity generation. Liquid biofuels contributed to 4 % in energy demand (Brown, Feuvre and IEA, 2017). Albeit the widespread of biogas technology, it is still economically less viable and hence requires various subsidies and incentive measures. European Union (EU) is the principal driver for the growth in incentives for the promotion of biogas supply chain. Due to the financial support from major EU countries, the feasibility of biogas production accounted for 79.4 % of OECD production in 2015. Biogas is sustainable and does not deplete the earth natural resources as compared to conventional energy sources such as natural gas.

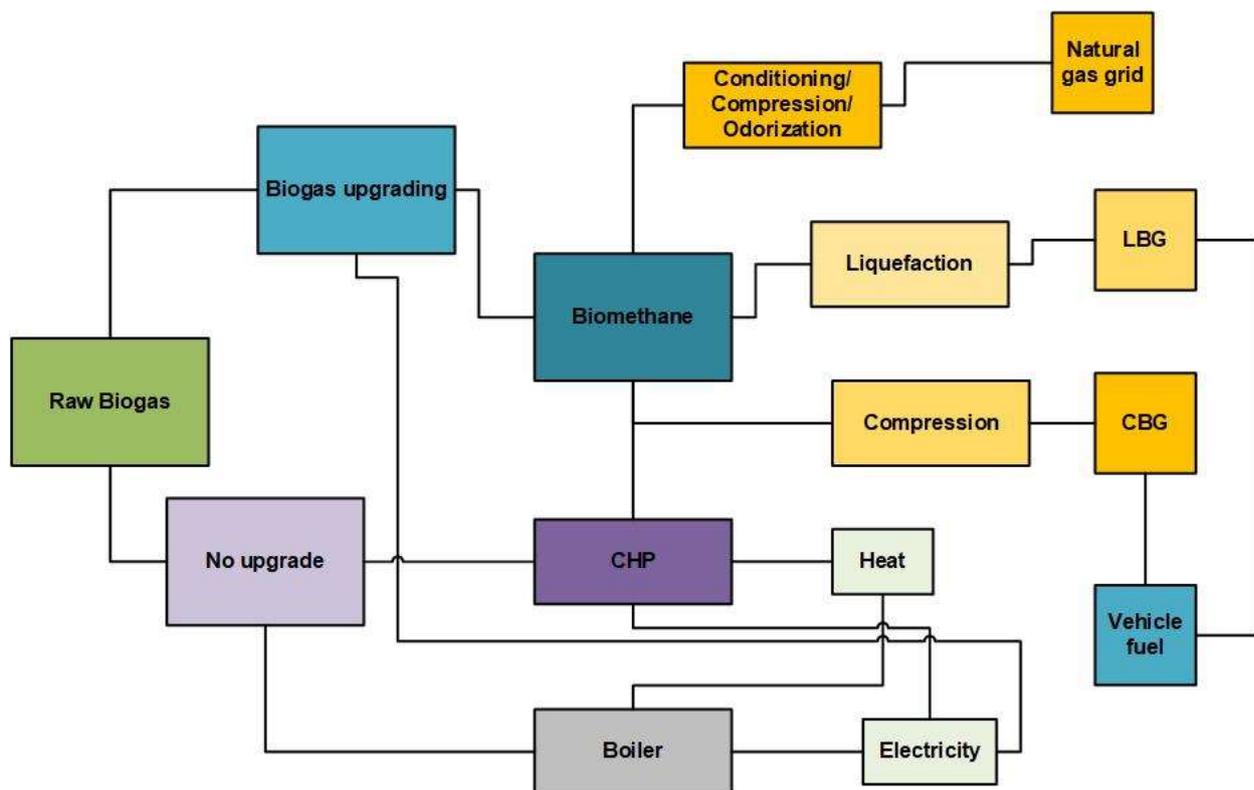


Figure 2.1 Various forms of Biogas utilization pathways. Biogas upgrading to natural gas quality is the scope of this study.

The energy content of biogas (mainly due to the presence of methane) is between 23 - 30 MJ/m<sup>3</sup> (Higher heating value) (Banks, 2009). This energy content of biogas is utilized in various forms such as the production of heat in boilers, co-generation units for heat

and power (CHP), or upgrading it to natural gas quality. Most European countries utilize biogas for internal energy purposes. In case of biogas plants, the heat produced from biogas is used for internal heating equipment such as digesters, pumps, etc. The electricity consumed by the biogas plant is relatively low, and hence the extra electricity produced is transported to the grid. Also, the heat is transported via district heating networks. Figure 2.2 shows the utilization of biogas published by Swedish energy agency in the year 2010. Three major factors that are critical in utilizing the bioenergy potential are a higher cost associated with feedstocks, availability of feedstocks, and the scarcity of innovations that are economically feasible

### **2.1.1 Biogas use in heat supply**

Biogas can be used as an alternative to natural gas when it meets the safety standards for gas utilization for burning purposes. Alternatively, in most developing countries, biogas is still utilized for cooking and lighting. Also, biogas can be burnt in boilers to produce steam. Combustion in boilers is more efficient as the tolerance for biogas for impurities is relatively high. Thus, biogas does not require an upgrade when used in boilers. The pressure is set to 8 to 25 mbar when used for steam production. Furthermore, it is advisable to reduce H<sub>2</sub>S content below 1,000 ppm to prevent corrosion. Removal of H<sub>2</sub>S occurs when the water vapor is evaporated as most of the dissolved H<sub>2</sub>S is removed simultaneously (Persson, Jonsson and Wellinger, 2007)

### **2.1.2 Biogas use in CHP**

Biogas in internal combustion engines is one of the most widely used engine technologies. It is an established technology, and the engine sizes range from 30 kW to 3,000 KW. Most of them are in use for large-scale application including diesel engines with 8-10 % diesel injection. The advantage of using internal engines is its ability to generate energy without upgrading. A typical engine can accommodate a mixture of Methane CH<sub>4</sub> and CO<sub>2</sub> concentration as low as 21 % (Arnold, 2010). They can achieve optimal combustion with 31 (mol %) CH<sub>4</sub> concentration. Small-scale engines have a fuel conversion to electricity within the range of 30 % to 40 % in which, spark ignition of 29 % and dual fuel engine has 31 % of electrical efficiency. Large-scale applications can attain a fuel efficiency of around 38 %. The thermal efficiency of CHP units is pretty high within the range of 45 to 60 %. A major part of biogas converts to heat which can be achieved using heat exchangers from exhaust heat. Thus, the overall efficiency of an internal combustion engine could attain 85 % with 15 % losses. According to chamber et al. (2002), these engines require a major haul of 5 years. Use of biogas in the sterling engine is accounted. These are known as an external combustion engine. The tolerant for biogas impurities is high due to its external combustion nature. The thermal efficiency of the sterling engine is high and can attain a high efficiency with mixed fuel. According to Electric power research institute (EPRI, 2006), the minimum heating value of a fuel to be used in the sterling engine is 12 MJ/m<sup>3</sup> which corresponds to 35 mol %

CH<sub>4</sub>. In practice, internal combustion engines occupy a major market in biogas utilization as compared to sterling engines. Gas turbines for biogas use are still limited due to its enormous power generation operation which is more than 5 MW in general. The major limiting factor is the concentration of CH<sub>4</sub>, although the upgraded biogas could be more efficient. Thus, there is a huge gap in economic profitability. Microturbines are the better version of gas turbines with good economic value. The typical capacity ranges below 500 KW and found in many energy operational facilities like landfill sites. Turbines are sensitive to gas impurities than gas engines

### **2.1.3 Biomethane from biogas**

Biogas, when upgraded, has a similar chemical composition or it is identical to natural gas. The upgraded biogas is known as “biomethane.” The technology itself is called as “biogas upgrading,” and it is suitable for energy purposes, such as use in heat and power production, the supply of gas to the grid or as a vehicle fuel. It is biogenic in origin as it is produced from biological waste such as energy crops, organic manure, food waste or sewage. According to European Biogas Association (EBA 2013), there were 367 biomethane plants with a total capacity of 1303 billion m<sup>3</sup> by the end of 2014, an increase of 23 % increase as compared to 2013. Germany has the highest number of biomethane fed in plants (178) followed by Sweden (59), the UK (37), Switzerland (24) and the Netherlands (21). The usage of produced biomethane depends on the specific country. In Germany, 87 % of biomethane is used in CHP for heat and power production. Thus, the use of biomethane is spatially separated, whereas, in the UK, an overwhelming part of biomethane is in supply to the gas grid due to the renewable incentive scheme (Horschig *et al.* 2016). Biomethane use contributes to greenhouse gas (GHG) emission reduction by substituting natural gas. Germany and the UK save approximately 2446 Kt CO<sub>2</sub> eq and 606 Kt CO<sub>2</sub> eq respectively substituting natural gas by biomethane. In the transport sector alone 20 % biomethane in the fuel mixture contributes to the reduction of a reduction of 24 g CO<sub>2</sub>/kWh. Vehicle fuel substituted with biomethane can reduce the emissions of GHG from 21 - 24 % compared to that of diesel fuel. (Zhang, 2013)

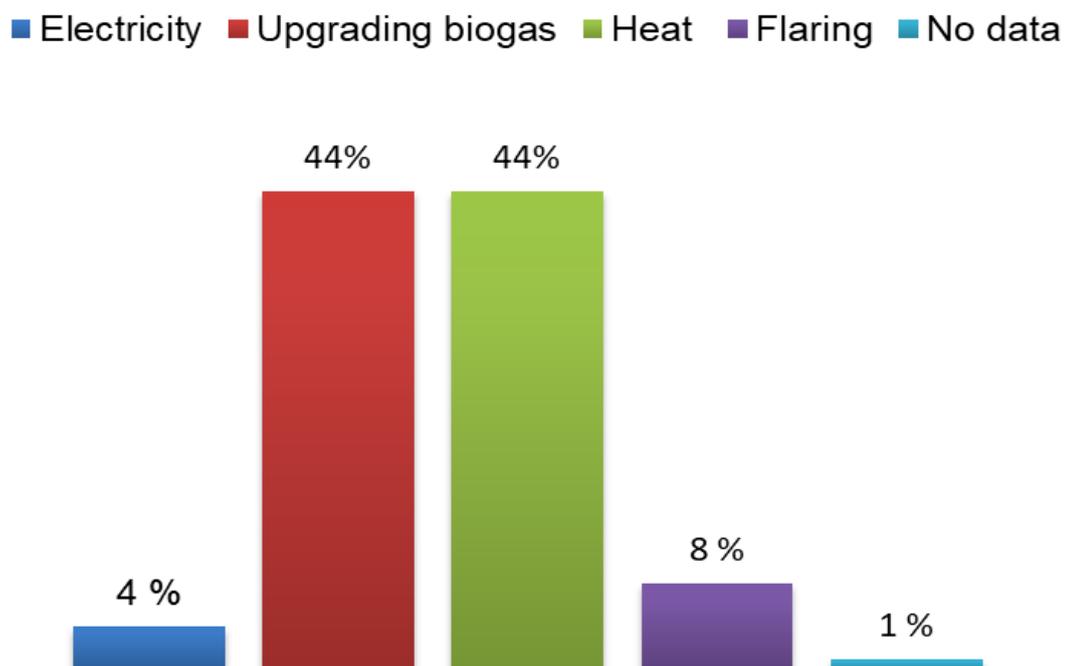


Figure 2.2: The proportion of biogas utilization showing major use in electricity generation followed by biogas upgrading, adopted from Swedish energy agency (Allegue and Hinge, 2012)

Besides its advantages, biogas upgrading has often been criticized for its high-energy consumption in bioenergy supply chain. This, in turn, might lead to high carbon emissions. The EU directive (2009/28/EG) adopted on 23<sup>rd</sup> April requires that EU member states should increase the use of energy from renewables. Especially, two directives, Renewable energy directive (European Parliament, 2009b) and Fuel Quality Directive (European Parliament, 2009a) indicate the limit of greenhouse gas emissions (GHG) emissions with sustainability criteria. This limit has to be to be 50 % from 1 January 2017. These concerns the biogas upgrading industry as the second highest carbon emission comes from biogas upgrading.

#### 2.1.4 Biomethane in the natural gas grid

Biogas can be fed into natural gas grid after it undergoes necessary treatment. The treatment process includes removal of carbon dioxide, hydrogen sulfide, moisture and other minor impurities. As a result, it is upgraded to a natural gas quality called "biomethane." Biomethane typically contains greater than 95 % vol of methane. Various technologies can offer unto diverged amount of methane content in biomethane. It is a great substitute for natural gas and is used in natural gas pipelines for various purposes. According to the study (Willumsen, 2008), landfill gas was initially used to upgrade to natural gas quality in the Netherlands in 1995. The reason behind upgrading biogas is that the increase in methane content which is in turn directly

proportional to the heating value. One important factor in determining the gas quality is the “Wobbe index.” Higher heating value denotes the energy released during the combustion of one normal cubic meter of biogas when the water is condensed. Lower heating value denotes the energy released during combustion of 1 m<sup>3</sup> of biogas when water vapor is not condensed.

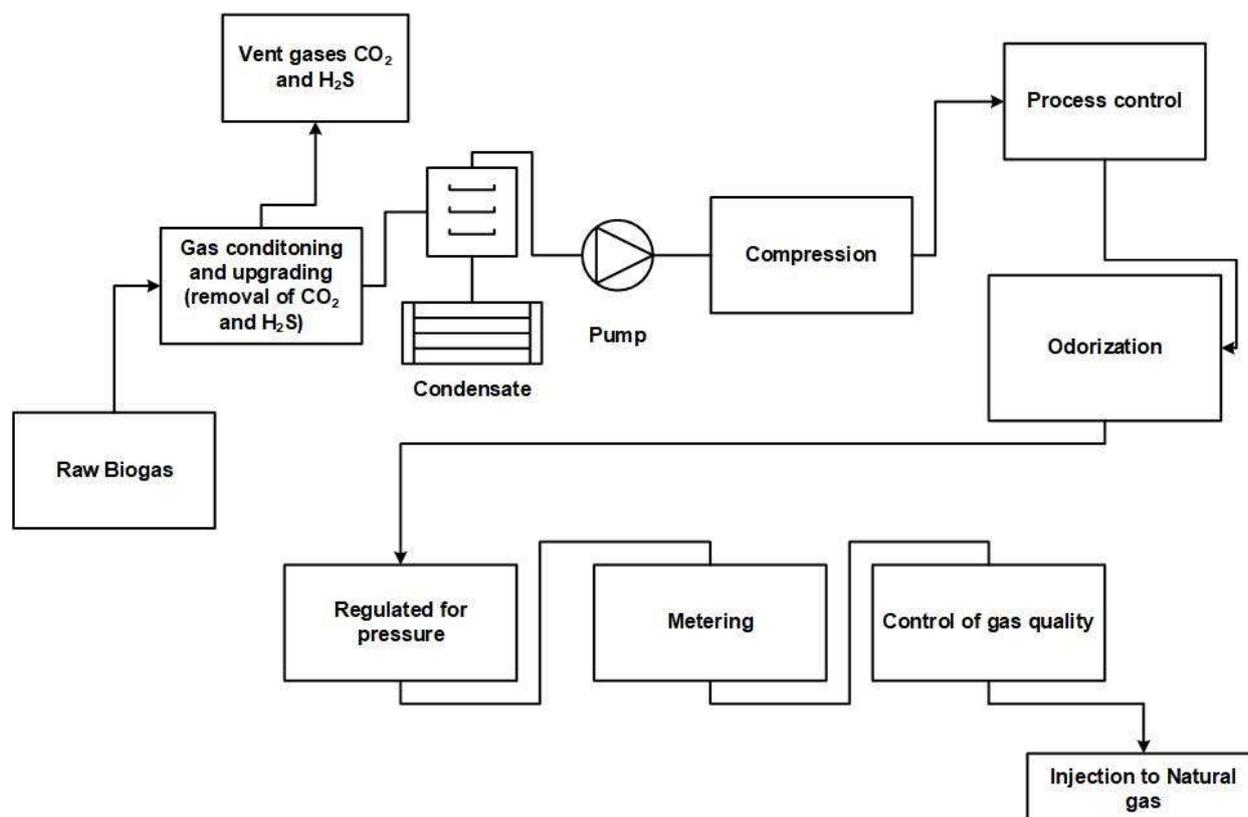


Figure 2.3: Typical layout of biogas conditioning and processing. Flow pathway of upgraded biogas injection into the natural gas grid.

Table 2-1: Standards of biomethane quality injection into the natural gas grid. Comparison of requirements from different countries (Allegue and Hinge, 2012)

Country	Austria	France	Germany	Netherlands	USA	Switzerland	British Colombia	California	Sweden
Physical properties									
Calorific upper value (MJ/m <sup>3</sup> )	38.5 - 46.1	38.5 - 46.1 (H gas) 34.2 - 37.8 (L gas)	30.2 - 47.2	31.6 - 38.7		38.5 - 47.2 (unlimited injection)		36.9 - 42.8	
Wobbe Index (MJ/m <sup>3</sup> )	47.9 - 56.5 (upper)	48.2 - 56.5 (H gas) 42.5 - 46.8 (L gas) (upper)	46.1 - 56.5 (H gas) 37.8 - 46.8 (L gas) (upper)	43.6 - 44.41 (upper)		47.9 - 56.5 (unlimited injection)	48.2 - 56.5 (H gas) L: 42.5 - 46.8 (L gas) (upper)	47.6 - 51.6 (upper)	44.7 - 46.4 (Type A) <sup>1</sup> 43.9 - 47.3 (Type B) <sup>1</sup> (lower)
Qualities									
CH <sub>4</sub> (%) <sup>b</sup>	> 96			> 80	93.5	(unlimited injection ) > 50 (limited injection)	> 95.5		97±1 (Type A) <sup>1</sup> 97±2 (Type B) <sup>1</sup> >
CO <sub>2</sub> (%) <sup>b</sup>	< 2	< 2.5 <sup>3</sup>	< 6	< 6 (< 10 - 10.3 for regional grid)	< 2	< 6 (unlimited injection ) < 4 (limited injection)	< 2	3	<3
CO <sub>2</sub> +O <sub>2</sub> +N <sub>2</sub> (vol %)									4 (Type A) <sup>a</sup> < 5 (Type B) <sup>a</sup>
H <sub>2</sub> (%) <sup>b</sup>	< 4	< 6	< 5	< 12	< 0.5	< 4		0.1	

O <sub>2</sub> (%) <sup>b</sup>	< 0.5	< 0.01 <sup>3</sup>	< 3	< 0.5	< 1	< 0.5	< 0.2	< 0.2	< 3
CO (%) <sup>b</sup>		< 2		< 1		< 0.5			
Total inert (vol.-%) (CO <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> , CO, H <sub>2</sub> )								4	
Water dew point (°C)	< -8 (40 bar)	< -5 at MOP <sup>4</sup>	Ground temperature	< -10 (8 bar)		-8 at MOP <sup>4</sup>			< t <sup>6</sup> -5 < -9 (at 200 bar)
Total sulfur (mgS/m <sup>3</sup> )	< 10	< 30	< 30 <sup>7</sup>	< 45	< 23	< 30		265	
H <sub>2</sub> S	< 5 mg/m <sup>3</sup>	< 5 mg/m <sup>3</sup> (H <sub>2</sub> S+COS)	< 5 mg/m <sup>3</sup>	< 5 mg/m <sup>3</sup> 8	< 10 ppm = < 15.2 mg/m <sup>3</sup>	< 5 mg/m <sup>3</sup>	4.3 ppm	88 mg/m <sup>3</sup>	4.1 ppm
Mercaptans (mg/m <sup>3</sup> )	< 6	< 6	< 6	< 10		< 5		106 mg/m <sup>3</sup>	
Carbonyl sulfide	< 5 mg/m <sup>3</sup>								
Ammonia	Technically free	< 3 mg/m <sup>3</sup>	< 20 mg/m <sup>3</sup>	< 3 mg/m <sup>3</sup>	< 20 mg/m <sup>3</sup>	< 20 mg/m <sup>3</sup>		< 0.001 mol %	
Halogen compounds	0		< 1 mgCl/m <sup>3</sup>			< 1 mgCl/m <sup>3</sup>		< 0.1 ppmv	
Chlorine compounds (mg/m <sup>3</sup> )	Technically free	< 1	Technically free	< 50					
Fluorine compounds (mg/m <sup>3</sup> )	Technically free	< 10		< 25					
Hydrogen chloride (ppm)	Technically free			< 1					

Hydrogen cyanide (ppm)	Technically free			< 10					
Siloxanes	< 10 total silicon mg/m <sup>3</sup>			< 5 ppm				Commercial free or < 0.1 mgSi/m <sup>3</sup>	
BTX (ppm)				< 500		≤ 50 (BTX + PAC)			
Aromatic hydrocarbon (mol.-%) < 1				< 1					
Aldehydes, ketones (ppmv)								< 0.1	
PCBs (ppb)								< 0.1	
VOCs(ppmv)								< 0.1	
Dust	Technically free	< 5 mg/m <sup>3</sup>		Technically free	< 1 μm	Technically free		Free	
Heavy metals including Hg		< 1 μm/m <sup>3</sup> Hg	< 5 mg/m <sup>3</sup>			< 5 mg/m <sup>3</sup>		0.01 μm/m <sup>3</sup> Hg	
Volatile metals (μg/m <sup>3</sup> )								0.01	
Pesticides (ppb)								< 1	
Water content max. (mg/m <sup>3</sup> )				< 32			< 65		< 32

a) Type A and B refers to biomethane vehicle fuel with different engines

b) Gases are indicated using vol % or mol %; both are relevant

Thus, in European countries, the natural gas Wobbe index is divided into H (high-value gas) and L (low-value gas). Wobbe index of biomethane is altered by the addition of propane or butane (Wheeler *et al.* 1999). This alteration of biogas is called “conditioning of biogas” with natural gas. Conditioned biogas will have a variety of heating value than natural gas. In general, the minimal volume of biomethane is usually added to the gas grid with a high volume of natural gas. Once upgraded, biomethane fed into the natural gas network should be adjusted for appropriate pressure in the grid. In general, a pressure of 1 bar is recommended for household gas supply. Various upgrading technologies offer biomethane with variable pressure. The gas pressure also varies with different end-user needs such as industrial process, CHP, and vehicle fuel gas grids. Thus, the natural gas grids with biomethane supply work in the range of 4 bar. Biomethane and natural gas are usually odorless, and hence it is also conditioned with signal gas as adoration. The injection points, pressure, and quantity vary, and the cost depends on the above factors. The various steps in biomethane addition to the existing natural gas network are shown in figure 2.3.

While feeding upgraded biogas to natural gas network, it is important to notice that the gas quality meets the requirements of local quality standards. There is no international technical standard for biogas injection, but many countries do have national standards for biogas injection (see table 2-1).

Table 2-2: European countries with national regulations on biomethane from biogas (Allegue and Hinge, 2012)

Country	Regulation on biomethane	Remark
Austria	Directive ÖVGW G31 (2001) on gas composition and G33 (2006) on injection of biogas based on renewable gases into the natural gas grids. ÖVGW G79 sets requirements on odorization.	Not allowed to inject biogas from landfills or sewage gas
France	National guidance n°2004-555 (2004) and technical specifications AFG B562-1 and B562-2 for the distribution and transportation grid respectively.	Sewage sludge substrates and industrial waste are excluded for grid injection. However, this situation might change in a close future.
Germany	Standards DVGW G260 (2008) on gas composition, G262 (2004) on injection of renewable gases in public grids, G 280-1 and G 280-2 on odorization	The rules offer the possibility of feeding biomethane as an additional gas. This implies that biomethane of different heating valued can be fed into the grid as long as the resulting gas quality is in line with the specifications.
Netherland	Gas Act of the Netherlands for local gas grids (2006)	It is allowed grid injection of biomethane from all feedstock including landfill. The experience from the Netherlands using grid injection of landfill gas is positive, and there have not been any publicized problems or system

		failures
Sweden	Standard SS155438 (1999)	Sweden developed a national standard for biogas as a vehicle fuel on request of the Swedish vehicle manufactures. This standard is also applied when injecting biogas into the natural gas grid.
Switzerland	Directive SVGW G13-09 (2008) on gas quality requirements. Technical standards SVGW G11 on odorization and SVGW G 209 on the technical realization of the grid connection.	Two different qualities are allowed in the Swiss regulations: gas for limited injection (cleaned raw biogas, CH <sub>4</sub> > 50 %) and gas for unlimited injection (CH <sub>4</sub> > 96 %) The original G13 was developed in 2004 and modified in 2008 with the inclusion of ammonia, heavy metals, and halocarbon limits, and is under further review to focus on additional requirements for limits on the siloxanes content of the NCS gas. It is not allowed to inject biogas from landfills
Poland	Polish Standards PN-C-04752:2011 and PN-C-04753:2011	Landfill and sewage gas are restricted from the grid

Internationally, Canada and USA also have gas quality requirements (See table 2-2). In North America, there are efforts undertaken to execute single standard for biomethane injection (BC Innovation Council, 2008). In Europe, many countries such as Germany, Sweden, Austria, Denmark, etc. inject biogas into the natural gas grid and have also developed detailed specific standards for biomethane injection. It is worthwhile to mention Germany commitment to biomethane production and injection into the natural gas grid. Germany has developed the national standard based on the German standard for natural gas (DVGW) for biomethane injection (G262). It is the merging of two cooperation that includes German Water and Gas Association and the German Biogas Association. Also, the countries commitment to biofuel production has resulted in 165 biomethane plants in connection with grid injecting 106,800 m<sup>3</sup>/h biomethane in 2015. (Einspeisekapazität der Biomethane-Anlagen in Deutschland bis 2014). A significant part of biomethane is used in CHP plants (87 %), as fuel (4 %) and for heat export (9 %) (Thomas et al. 2016). This is mainly due to the EU renewable and sustainability policy. Besides the EU laws, Germany also has developed various support schemes and a plurality of laws for biomethane injection into the natural gas grids. The predominant use of biomethane in the gas grids is the result of Renewable energy act "EEG" (Energien, 2017) and the German energy industry act (EnWG). The injection of biomethane into the gas grids is moderated by German gas suppliers from the ordinance on Gas Network Access ('Verordnung über den Zugang zu

Gasversorgungsnetzen (GasNZV, 2010). Few support schemes include that the gas grid operator bears the significant cost of connection (75 %) from biomethane plant to gas grid as “Avoided network fee” as a bonus for biomethane injection etc. In contrast to German biomethane market, UK has developed a generous feed-in tariff for biomethane injection into the grid. Thus, Europe leads worldwide in biomethane injection into gas grids. Various EU institutions such as gas networks (CEN/TC 234/WG 9) and common standard on fuel (CEN TC 19) are formulated to develop a common standard for biomethane injection within EU. Important organizations include Marcogaz Technical Association of the European Natural Gas Industry, KIWA Gas Technology in 2007, ENTSOG, AFSSET (French National Health Agency), (Huguen *et al.*, 2010) (Devine-wright, 2013) (Spijker, 2014)

## 2.2 Biogas upgrading technologies

Biogas upgrading has gained attention in oil and natural gas prices and has become competitive in many countries. According to International energy agency (IEA), various biomethane plants are rising in increased proportion (IEA bioenergy task 37). Biogas upgrading by definition is the removal of carbon dioxide from biogas to produce a gas with high methane content (greater than 96 %). It also includes removal of contaminants such as H<sub>2</sub>S, NH<sub>3</sub>, O<sub>2</sub>, H<sub>2</sub>O present in the biogas. Many institutions have come forward in developing upgrading technologies that are technically compatible and cost-effective. Few of them include IEA bioenergy, Swedish Gas technology center (SGC). Various upgrading technologies offer various biomethane quality at the outlet depending on the end use. Upgrading of biogas consumes a reasonable amount of energy and adds up to the cost of biogas production. There are also methane emissions or methane slip during the upgrading process, which might cause greenhouse gas emissions. While technically achievable at all scales, these upgrading technologies suffer a setback in small-scale industries due to high cost and energy consumption (Bauer *et al.* 2013b). The report on biogas Seventh framework programme theme "Biowaste as feedstock for a 2nd generation", (2010) stated that in Europe, a high percentage of the total biogas production comes from many small-scale digesters (50 - 200 m<sup>3</sup> hour<sup>-1</sup>) producing small quantities of biogas. The upgrading cost for small-scale plants (<100 m<sup>3</sup> hour<sup>-1</sup>) is around 0.03 - 0.04 € kWh<sup>-1</sup>, (Björn and Lars, 2007) and for large plants (200 - 300 m<sup>3</sup> hour<sup>-1</sup>), it is 0.01 - 0.16 € kWh<sup>-1</sup>. Hence, it is ideal to select an appropriate technology for any given end use. The below section describes the technical features of various upgrading technologies currently operated worldwide.

## 2.3 CO<sub>2</sub> removal techniques

### 2.3.1 Pressure swing adsorption (PSA)

Pressure swing adsorption (PSA) is used to separate CO<sub>2</sub> from biogas using physical properties. The central principle is adsorption and is accomplished by an adsorbent on a porous bed material. During the process of upgrading, biogas passes from the bottom

of the reactor under elevated pressure. The adsorbent adsorbs CO<sub>2</sub> selectively whereas CH<sub>4</sub> relatively has larger molecular size and hence passes through the porous bed freely. It is captured at the outlet as enriched biomethane (>90 %). When the adsorbent bed is saturated, the pressure reduces, and the adsorbed CO<sub>2</sub> molecules are released as off gas. Many adsorbent materials are currently used for this technology. Few include activated carbons (Rashidi, Yusup, and Hon, 2013), natural and synthetic zeolites, silica gels and carbon molecular sieves (CMS) (Bauer *et al.* 2013a). There are also innovative materials for adsorption such as metal-organic frameworks (MOFs). The adsorbent bed in PSA could be permanently destroyed as it adsorbs H<sub>2</sub>S irreversibly (Hoyer *et al.* 2016). Hence an H<sub>2</sub>S pretreatment set up is required for PSA unit in operation. In case of high purity requirement, higher CH<sub>4</sub> is loss occurs, and the vent gas requires post-treatment (Thrän *et al.* 2014). Several columns operate in parallel to increase the methane yield. However, this might lead to complexity and high capital cost. Hence an optimal requirement without compensating the gas purity is required. Alternatively, various new techniques for PSA process are in research as reported by BC Innovation Council (Electrigaz Technologies Inc, 2008). The concentration of CH<sub>4</sub> reaches up to 96 - 98 % (Moss *et al.* 2017). The methane losses are about 2 - 4 % (Petersson and Wellinger, 2009). The electricity consumption is about 0.25 kWh/m<sup>3</sup> raw biogas. The process is a dry method and demands no heat. Companies assume a lifetime of 10 years. Biogas plants with PSA technology range from 10 to 2,000 m<sup>3</sup> raw biogas/h (Allegue and Hinge, 2012)

### 2.3.2 Pressure water scrubbing

Pressure water scrubbing is most widely used technology for biogas upgrading. It is an absorption process where water is used as a solvent to absorb CO<sub>2</sub>. The process under pressure at around 6 -12 bar (Beil, Hoffstede and Hahn, 2010). Typically, packed columns are used for water scrubbing. During the process, biogas flows from the bottom to the top, and water flow is made countercurrent to biogas flow. The solubility of CO<sub>2</sub> is much higher than CH<sub>4</sub>, and hence CO<sub>2</sub> is dissolved in water and dissolved wet leaves at the bottom. Enriched biomethane collects at the top. The scrubbed water stream is regenerated in a desorption column separately. The regenerated CO<sub>2</sub> is released into the atmosphere as off gas. Water scrubbing is highly resistant to impurities especially H<sub>2</sub>S as the solubility of H<sub>2</sub>S in water is higher than CO<sub>2</sub> (Sun *et al.* 2015). The allowed concentration of H<sub>2</sub>S ranges from 300 - 2500 ppm. Since the dissolved H<sub>2</sub>S can cause corrosion problems, it is usually recommended to remove H<sub>2</sub>S before Pressure water scrubbing. The electricity consumption is 0.25 - 0.25 kWh/m<sup>3</sup> raw biogas and methane recovery is 99 % in some manufactures specifications. CH<sub>4</sub> purity is 98 %. Installations from 500 - 2,000 m<sup>3</sup>/h are found elsewhere.

Table 2-3: Comparison of different commercial upgrading technologies (Allegue and Hinge, 2012)

Parameters	PSA	Water scrubbing	Physical scrubbing	Amine scrubber	Membrane separation	Cryogenic
Electricity consumption (kWh/m <sup>3</sup> ) raw biogas	0.23 - 3.5	0.25 - 0.3	0.2 - 0.31	0.01 - 0.15	0.18 - 0.21	0.20 - 1.05
Electricity consumption (kWh/m <sup>3</sup> ) cleaned biogas	0.29 - 0.43 0.3 - 1.0 0.5 - 0.6 according to Swedish plants	0.4 (0.3 - 0.6) With regeneration 0.45 - 0.9 No regeneration 0.45 - 0.9	0.4 (Selexol)	0.2 - 0.25	0.14 - 0.26	0.63 - 0.8  1.4 (Acirion)1.54 (Prometheus)
Heat consumption raw biogas ((kWh/m <sup>3</sup> )	None	None	< 0.21	0.5 - 0.75	None	None
Heat demand (°C)	None	None	55 - 80 °C	100 - 180 °C	None	None
CH <sub>4</sub> losses (%)	2 - 5	1 - 2	2 - 4	0.1 - 0.2	15 - 20 (without using residue gas)	< 0.5
Pre-purification	Yes	Recommended roughly	Recommended roughly	Yes	Recommended	Yes
H <sub>2</sub> S co-removal	Possible	Yes	possible	contaminant	possible	contaminant

N <sub>2</sub> and O <sub>2</sub> co-removal	Possible	No	No	No	Partial	N <sub>2</sub> possible
Operation pressure (bar)	3 - 5 4 - 7 6 - 8 4 - 10	4 - 7 4 - 10	4 - 7 4 - 8	Atmospheric	5 - 7 6 - 8	17 - 26 (GtS)
Pressure at outlet (bar)	4 - 5	7 - 10	1.3 - 7.5	4 - 5	4 - 6	
CH <sub>4</sub> recovery (%)	83 - 99 < 96 > 96	< 97 > 97 98.5 96 - 98	93 - 97 > 97 > 99	97.5 - 99.5 99.9 >99 > 99.5 95 - 98	90 - 98 82 90 90 - 93.5 96 - 98 99	98 97

### 2.3.3 Chemical Scrubbing

Chemical scrubbing for biogas upgrading utilizes organic solvents as absorbers for CO<sub>2</sub>. Most commonly used solvents are amines such as monoethanolamine (MEA) or dimethylethanolamine (DMEA). Since the selectivity of amines with CO<sub>2</sub> is high, there is minimal loss of CH<sub>4</sub> (0.1 - 0.2 %). The purity of CH<sub>4</sub> is very high as 99.5 % can be reached at the outlet. The chemical scrubbing represents similar regenerative columns as water scrubbing. Chemical solvents are highly toxic, costly and non-environmental friendly, and hence regeneration is a must to reach the environmental standards.

However, there is very high heat demand for amine regeneration, and hence the energy consumption for the whole process is higher. Typically, cleaned biogas with the volume of around 0.5 kWh/m<sup>3</sup> is needed to generate amines in desorber columns. Pretreatment of H<sub>2</sub>S is required to avoid complex issues in operation (Niesner, Jecha, and Stehlík, 2013) and by (IEA, 2016) indicate that Chemical scrubbing is the most widely used technology.

It should be noted that Chemical scrubbing is most cost competitive if the heat demand is not met by on-site production (Al Mamun and Torii, 2015)

### 2.3.4 Membrane Technology

Membrane technology has evolved into a mature technology over the past few years and had many advantages such as low cost, energy efficient and compact module process. Due to the permeating ability of the membranes, CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, NH<sub>3</sub> and other components are separated from CH<sub>4</sub>. The CO<sub>2</sub> stream is called the permeate side and CH<sub>4</sub> is called the retentate stream. Different membranes are commercially available, and the driving force behind this process is a difference in partial pressures. The membranes are of two classes namely, gas-gas separation, gas-liquid separation. It is also divided into high pressure and low-pressure operation. The most used material for commercial applications is hollow fibers (Ryckebosch, Drouillon, and Vervaeren, 2011). Scholz (2014) studied membranes extensively and found polyamide and acetate-based membranes to be more economical. The membrane system is usually multistage process as single separation cannot achieve high purity CH<sub>4</sub>. Value of CH<sub>4</sub> purity in multistage systems is 99 %. The energy consumption is around 0.3 kWh/m<sup>3</sup> as given in table 2-3.

### 2.3.5 Cryogenic separation

Cryogenic upgrading uses different boiling points and sublimation point of gases as a principle to separate the unwanted gases from biogas. This process is exciting as it has many advantages such as, no addition of chemicals, purified CO<sub>2</sub> for trade, option to liquefy biomethane for Liquefied biomethane supply. It makes use of low temperatures to achieve various condensation of a mixture of gases. The operation temperature is usually below - 50°C. (approx. 220 K). During the process, the raw biogas passes into

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various compression and the cooling process followed by separation of liquid gases. Subsequently one of the major components in biogas mixture is CO<sub>2</sub>, and hence most of the cryogenic units are designed to remove CO<sub>2</sub> through condensation completely. Thus, the outlet containing high CH<sub>4</sub> purity is collected. There are also process that can liquefy biomethane with an intention to produce Liquid biomethane (LBG). Other impurities such as water, siloxanes are also removed during this separation process. It is also possible to separate nitrogen in the process. Various companies have already commercialized this technique such as Acrion technologies (Krich *et al.* 2005) from the US. They are actively involved in landfill gas separation to produce compressed biogas or LBG. The methane slip of the process is claimed to be 0.03 %. Since the pressure of the process is around 200 bar, it might result in high energy consumption. Some studies specify 5 -10 % of the cleaned biogas (Allegue and Hinge, 2012); (Seifert, 2013). The methane purity is relatively high up to 98 % (Hulu J *et al.*, 2008)

Table 2-4: Advantages and disadvantages of diverse commercial upgrading technologies (Allegue and Hinge, 2012)

Technology	Advantages	Disadvantages
PSA	<ul style="list-style-type: none"> <li>- Low energy use: high pressure, but regenerative</li> <li>- No chemicals</li> <li>- No heat demand</li> <li>- Relatively cheap technology</li> <li>- Compact technique</li> <li>- Also for small capacities</li> <li>- Many references in operation</li> <li>- Adsorption of N<sub>2</sub> and O<sub>2</sub></li> </ul>	<ul style="list-style-type: none"> <li>- Medium methane contents in the biomethane</li> <li>- High/medium methane losses</li> <li>- Components like H<sub>2</sub>S and water have to be removed before the process</li> <li>- Extensive process control needed</li> <li>- CH<sub>4</sub> losses when malfunctioning of valves. Often use of valves</li> </ul>
Water scrubbing	<ul style="list-style-type: none"> <li>- "Simple technology."</li> <li>- Cheap</li> <li>- Most references in operation</li> <li>- Co-removal of ammonia and H<sub>2</sub>S when H<sub>2</sub>S &gt; 300/500 ppmv (tolerance for impurities)</li> <li>- Easy in operation</li> <li>- Capacity is adjustable by changing pressure or temperature</li> </ul>	<ul style="list-style-type: none"> <li>- Requires much water, even with the regeneration process</li> <li>- H<sub>2</sub>S damages equipment (if &gt; 300/500 ppmv)</li> <li>- Medium methane contents</li> <li>- High/moderate methane losses</li> <li>- Clogging due to bacterial growth</li> <li>- Foaming possible</li> <li>- Low flexibility toward variation of the input gas</li> <li>- Biomethane drying necessary</li> </ul>

Physical scrubbing (glycol)	<ul style="list-style-type: none"> <li>- High methane content</li> <li>- Energetic more favorable than water</li> <li>- Relatively low CH<sub>4</sub> losses</li> <li>- Co-removal of ammonia, H<sub>2</sub>S, and other impurities, but a rough pretreatment is recommended.</li> </ul>	<ul style="list-style-type: none"> <li>- Relatively expensive investment and operation</li> <li>- Difficult in operation. Incomplete regeneration when stripping/vacuum (boiling required)</li> <li>- The reduced operation when dilution of glycol with water</li> </ul>
Chemical absorption (amines)	<ul style="list-style-type: none"> <li>- High methane content efficiency</li> <li>- Low electricity demand</li> <li>- Process without pressure</li> <li>- More CO<sub>2</sub> dissolved per unit of water, compared to water</li> <li>- Shallow CH<sub>4</sub> losses</li> <li>- No moving components (except blower)</li> </ul>	<ul style="list-style-type: none"> <li>- Relatively expensive investment</li> <li>- High heat demand regeneration</li> <li>- Corrosion</li> <li>- Decomposition and poisoning of the amines by O<sub>2</sub> or other chemicals</li> <li>- Precipitation of salts</li> <li>- Foaming possible</li> <li>- H<sub>2</sub>S pre-removal normally necessary</li> </ul>
Membrane technology	<ul style="list-style-type: none"> <li>- Simple construction, low weight, and small footprint.</li> <li>- Simple operation, no moving components except blower. Low maintenance</li> <li>- Modular configuration even for low volume rates</li> <li>- No chemical or heat demand</li> <li>- High reliability</li> <li>- Small gas flows treated without a proportional increase in costs</li> <li>- Gas/gas: H<sub>2</sub>O is removed</li> <li>- Gas/liquid: cheap investment and operation; pure CO<sub>2</sub> can be obtained</li> </ul>	<ul style="list-style-type: none"> <li>- Low membrane selectivity: a compromise between purity of CH<sub>4</sub> and amount of upgraded biogas</li> <li>- Multiple steps required to reach high purity</li> <li>- Middle methane content</li> <li>- Middle to high CH<sub>4</sub> losses depending configuration</li> <li>- Little operational experience with improved membrane technologies</li> <li>- Membrane durability unsure</li> <li>- H<sub>2</sub>S removal step needed</li> <li>- Not suitable for biogas with many undefined contaminants, like landfill gas or biogas from WWTP</li> <li>- Membranes can be expensive</li> </ul>
Cryogenic separation	<ul style="list-style-type: none"> <li>- High CH<sub>4</sub> content can be reached</li> <li>- Low methane losses</li> <li>- CO<sub>2</sub> as by-product</li> <li>- No chemicals</li> <li>- Low extra energy cost to reach liquid biomethane (LBM)</li> </ul>	<ul style="list-style-type: none"> <li>- Relatively expensive investment and operation</li> <li>- H<sub>2</sub>S, siloxanes and other impurities removal step customarily needed.</li> <li>- Technically very demanding</li> <li>- Full-scale implantation very recent, so energy efficiency and technology is not well proved</li> </ul>

### 2.3.6 CO<sub>2</sub> capture and carbon capture and storage (CCS) techniques

According to the report from The Intergovernmental Panel on Climate Change (5th Assessment Report (AR5)) (IEA, 2012), it is confirmed that the global warming and climate change has been dramatically associated with greenhouse gas emissions. It is stated that to avoid worst effects; it is necessary to reduce CO<sub>2</sub> emissions globally by 41 - 72 % by 2050. (Leung, Caramanna, and Maroto-Valer, 2014). The process of capturing and storing CO<sub>2</sub> originating from biomass is called as Bio-CCS (VDB, 2010). These are applied to all energy production process where CO<sub>2</sub> rich process streams are liberated. Biomass that emits CO<sub>2</sub> during the conversion process can be captured and stored permanently in geological or mineral form.

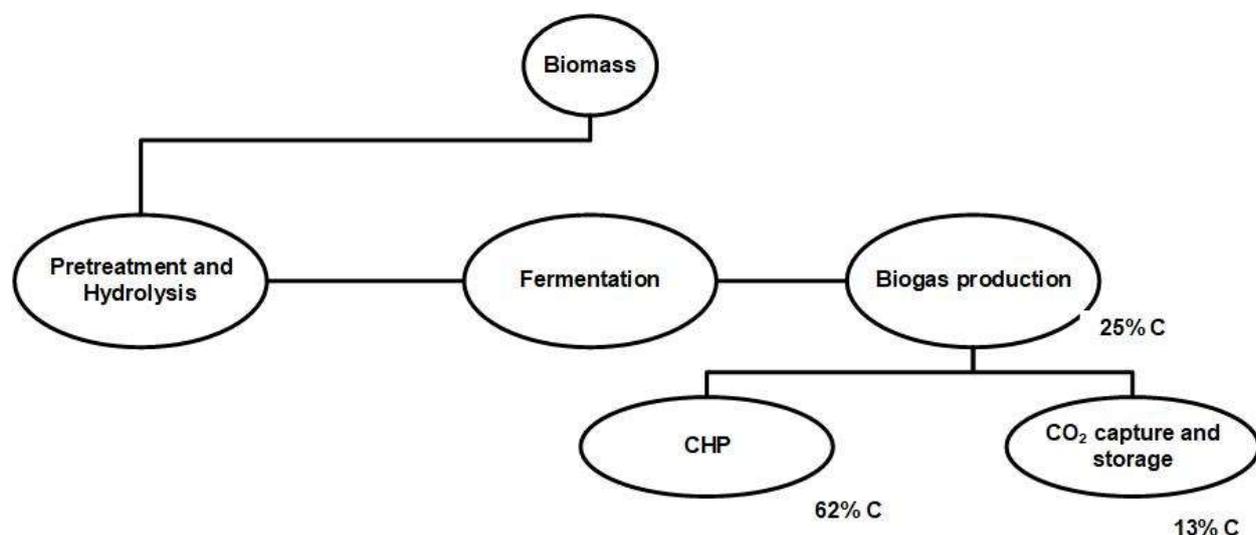


Figure 2.4: Distribution of carbon emission from biomass to energy generation. (ZEP, 2012)

This storage of carbon will result in less CO<sub>2</sub> emissions as they are not released into the atmosphere. World organizations which are actively involved in CCS technology include the IPCC's Special Report on Renewable Energy Sources and Climate Change Mitigation, the IEA and the United Nations Industrial Development Organization (UNIDO). Bio-CCS has also been recognized in European policy debate. The two major organizations in European bio CCS include European Technology Platform for Zero Emission Fossil Fuel Power Plants known as the "Zero Emissions Platform" (ZEP) and European Biofuels Technology Platform (ZEP, 2012). It recognizes that CCS "combined with biomass could deliver "carbon negative" value as found in figure 2.4. During biofuels conversion, a significant quantity of CO<sub>2</sub> present in the biomass is transferred to biofuels or biochemical. In biomethane production from anaerobic digestion, this CO<sub>2</sub> is often separated for better fuel quality. Though CO<sub>2</sub> separation techniques are

commercially established, it does face an inevitable challenge for storage in contrast to CCS. Though the impact of CO<sub>2</sub> capture and storage of biofuels is less compared to fossil fuels, there is still a more significant opportunity to implement Bio-CCS in various large industrial operations. The technical feasibility of implementing bio CCS technology depends on various factors such as availability of sustainable biomass, CO<sub>2</sub> storage capacity, the performance of CO<sub>2</sub> storage technologies. It also depends on the net energy conversion, including the CO<sub>2</sub> capture and storage and the net removal of CO<sub>2</sub> emissions from the plant. So far, there are two technologies in biogas upgrading implemented for this purpose and still in research scale. They are mineral carbon sequestration that employs, chemical industrial wastes and municipal bottom ash residues for CO<sub>2</sub> capture and storage.

## **2.4 CO<sub>2</sub> capture using Bottom ash**

### **2.4.1 Origin of bottom ash**

Municipal solid waste incineration is an efficient way of handling waste to produce energy. During incineration, energy in the form of heat and electricity is recovered (Cimpan and Wenzel, 2013). It is popularly termed as waste-to-energy technology and is increasingly used in major countries to handle waste. Municipal incineration reduces the volume of the waste and its mass by 70 %. The end products are bottom ash, fly ash, boiler ash, etc. Bottom ash is the most significant product of incineration and amounts to 80 % (Chimenos *et al.* 2005). According to CEWEP (2015) around 88 million tonnes of waste were treated in Waste-to-Energy plants in Europe. The amount of bottom ash produced was approximately 18 million tonnes. Bottom ash is a complex material composed of inert and non-combustible materials such as stone, brick, ceramic, glass and other unburnt organic matter (wood, fiber). A significant amount of metals is also found in bottom ash. The metals are usually extracted from the ashes and further recycled. Examples are aluminum, nonferrous materials. During incineration, the waste is fed into the furnace operating at a high temperature at around 850 °C. A substantial amount of air is supplied to ensure complete combustion of waste. After the incineration is completed, the raw bottom ash is collected and transported to a reprocessing facility where metals, minerals, and nonferrous metals are separated. It is also crushed to ensure a certain particle size. The remaining combustible material is also removed. Finally, bottom ash is stored for a process called “aging” before being disposed of in landfills or used for other purposes including for road construction, filling material, aggregates, noise barriers, art supports, etc (Cewep, 2010)

### **2.4.2 Physical and chemical properties**

Various studies have been attempted to study the physical and chemical properties of bottom ash. Gorme *et al.* (2010) found that the bottom ash from MSWI could be utilized for road construction purposes. Its chemical properties were studied by Toller *et al.* (2009) and found that bottom ash contains heavy metals such as lead, copper,

antimony, etc which can be harmful to the environment during leaching. One main characteristic of bottom ash is its particle size distribution (PSD). Approximately, 70 % of bottom ash particles are in the range of 0.1 - 11.2 mm, similar to concert aggregates (EN 1260, 2008). Bottom ash also contains water as a result of quenching and outdoor storage. Tang, (2012) found that the bottom ash water content from a waste-to-energy plant located in Wijster, Netherlands varies from 13 % to 25 % (wet/dry weight percent). The density of bottom ash is usually around  $2.5 \text{ g cm}^{-3}$  and is lower than cement. However, the particle size is more substantial due to metals contents present in the bottom ash. The chemical characteristics of bottom ash are complex and heterogeneous.

Table 2-5: Maximum leaching of inorganic compounds for building materials (Tang, 2012)

Parameter	A shaped	Non-shaped	IBC building material [mg/kg d.m.]
Antimony (sb)	8.7	0.16	0.7
Arsenic (As)	260	0.9	2
Barium (Ba)	1500	22	100
Cadmium (Cd)	3.8	0.04	0.06
Chromium (Cr)	120	0.63	7
Cobalt (Co)	60	0.54	2.4
Copper (Cu)	98	0.9	10
Mercury (Hg)	1.4	0.02	0.08
Lead (Pb)	400	2.3	8.3
Molybdenum (Mo)	144	1	15
Nickel (Ni)	81	0.44	2.1
Selenium (Se)	4.8	0.15	3
Tin (Sn)	50	0.4	2.3
Vanadium (V)	320	1.8	20
Zinc (Zn)	800	4.5	14
Bromide (Br)	670	20	34
Chloride (Cl)	110,000	616	8800
Fluoride (F)	2500	55	1500
Sulphate ( $\text{SO}_4^{2-}$ )	165,000	1730	20,000

The primary elements in bottom ash are, Si, Fe, Ca, Al, Na, IS and C. They constitute about 80 - 90 % by weight. Most of them exist in the form of oxides such as  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  which collectively account for 88 % of the bottom ash (Bayuseno and Schmahl, 2010). The finer particles contain higher amounts of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and lower amount of  $\text{SiO}_2$ . According to Wiles (1996), the composition of elements in bottom ash is similar to basaltic and other geologic materials. The minor elements enriched in bottom ash include Mg, Ti, Cl, Mn, Ba, Zn, Cu, Pb, and Cr. Trace elements include Sn, Sb, V, MO, As, Se, Sr, Ni, Co, Ce, Ag, Hg, B, Br, F and I. The composition of major and most minor elements is similar to basaltic and other geologic materials. Apart from oxides, bottom ash also contains hard matter such as ferrous components, free metallic iron, and aluminum. Saikia *et al.* (2008) studied the mineralogical properties of bottom ash and found that significant amount of quartz ( $\text{SiO}_2$ ), Calcite ( $\text{CaCO}_3$ ), anhydrite ( $\text{CaSO}_4$ ), Gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ), magnate and hematite ( $\text{Fe}_2\text{O}_3$ ). Figure 2.5 shows the elemental composition of bottom ash.

### **2.4.3 CO<sub>2</sub> absorption with bottom ash**

Bottom ash mineralogical properties make them attractive as it can replace concretes or can be used for road and building construction purposes. However, to be used for those purposes, bottom ash should undergo treatment process to ensure environmental standards are met. This is mainly due to the leaching of heavy metals from bottom ash that has been reported worldwide. Specifically, heavy metals such as Cu, Pb, Zn have been reported to exceed Flemish limit values, a standard used for heavy metals leaching (Gerven *et al.* 2005). Table 2-5 shows the Flemish limit values heavy metals that could be safely exposed to the atmosphere.

The primary element exceeding the Flemish limit value is Cu for MSWI bottom ash. Leaching of other elements such as Ba, Mo, and Sb was also found in bottom ash. Various treatment options are available to avoid leaching of heavy metals in bottom ash. It is also called “aging of bottom ash” (Arickx *et al.* 2010)

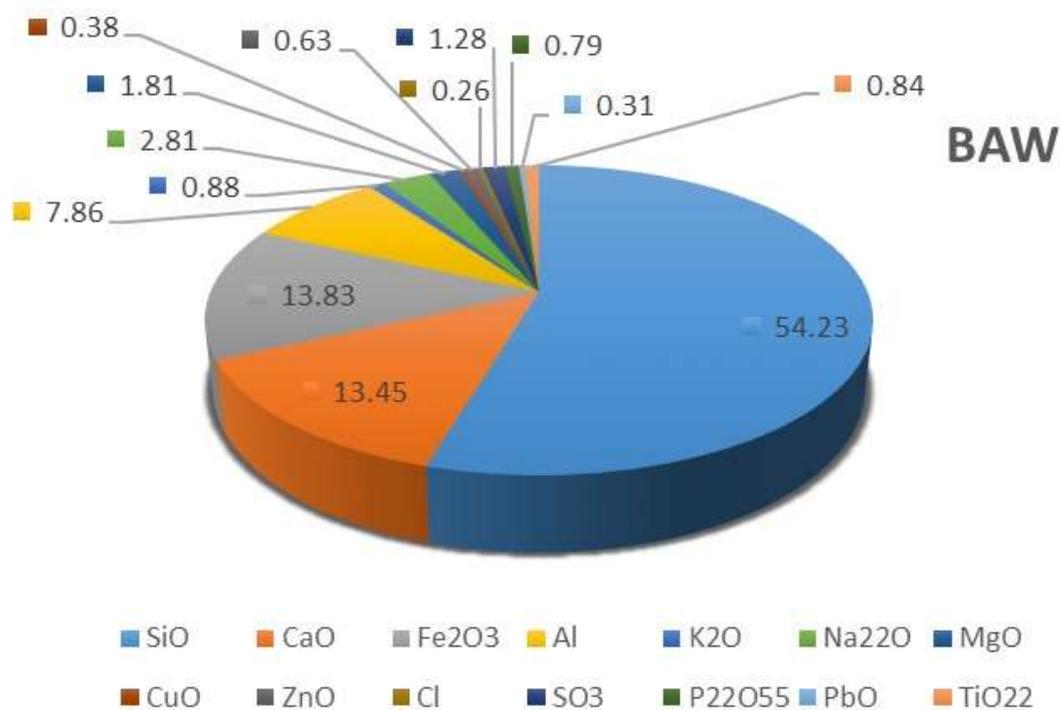
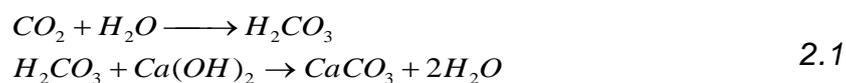


Figure 2.5: Typical distribution of minerals in bottom ash particle, adopted from (Tang *et al.*, 2015); (BAW = bottom ash weathered)

The most common methods employed for aging include oxidation, carbonation, neutralization of pH, precipitation of metals, etc (Arickx, Van Gerven and Vandecasteele, 2006). Carbonation is one the most widely used technique for the aging of bottom ash (Poletini and Pomi, 2004). Carbonation is described as a process in which CO<sub>2</sub> present in the atmosphere reacts with hydroxides of bottom ash, and results in the formation of carbonates. It is often a two-step process as described in the equation 2.1 (Onori, 2011)



The primary reaction is portlandite (Ca(OH)<sub>2</sub>) carbonation to the formation of stable calcite (CaCO<sub>3</sub>) in an aqueous medium. In the first step, CO<sub>2</sub> is absorbed into the water molecules present in the pores of bottom ash. The resulting bicarbonate reacts with the hydroxides of bottom ash to form carbonates and water. This reaction is accompanied by the decrease of pH from 11 -12 to 8 - 9 (Meima and Comans 1997). The formation of stable calcite (CaCO<sub>3</sub>) increases sample mass, which is in turn linked to the amount of trapped carbon dioxide (Rendek, Ducom, and Germain, 2006). In general bottom ash is stored in open place for 6 -12 weeks in the atmosphere to undergo natural carbonation process. Arickx *et al.* (2010) found that after three months of natural carbonation or aging, bottom ash underwent a significant carbonation reaction with the steady decrease in pH. It is interesting to note that bottom ash carbonation could be achieved

using a technique called accelerated carbonation where CO<sub>2</sub> rich streams pass through bottom ash under a particular pressure to achieve carbonation in lesser time. This has been proven by using stack gas as an example by Arickx, Van Gerven, and Vandecasteele, (2006) and confirmed that it is advantageous as it also reduced CO<sub>2</sub> emissions.

## 2.5 H<sub>2</sub>S toxicity and its removal techniques in biogas

The emission of a volatile reduced sulfur compound such as hydrogen sulfide (H<sub>2</sub>S) can be problematic due to its corrosive nature and foul smelling in biogas plants. The process of removal of H<sub>2</sub>S from biogas is called desulphurization. Its concentration varies from 0.1 - 2 (vol %) depending on biomass protein content (Ramírez *et al.* 2011). Sulfate-reducing microorganisms present in the biomass produces H<sub>2</sub>S during anaerobic digestion. The toxicity of hydrogen sulfide is known worldwide. Table 2-6 below presents the Physical and chemical properties of hydrogen sulfide (EPA, 2010).

Table 2-6: Physical and chemical properties of hydrogen sulfide

Properties	Data
Chemical symbol	H <sub>2</sub> S
Molecular weight	34.08 g/mol
Appearance and color	Colorless gas
Odor	Rotten egg
Relative density Gas @ 101.325 kPa 25 °C	1.188
Specific volume at 21.1 °C	70.11 dm <sup>3</sup> /kg
Melting point	-86 °C
Occupational exposure hazard	10 ppm TLV

Biogas application is limited due to the corrosive nature of Hydrogen sulfide in equipment such as pipelines, engines, gas storage tanks, etc.

When Hydrogen sulfide is not treated, a substantial amount of sulfur dioxide emissions is exposed to the atmosphere which is environmentally harmful. Due to extreme adverse effects of hydrogen sulfide in biogas, it is usually removed before biogas is upgraded to biomethane. The primary approach employed for H<sub>2</sub>S removal are physical and chemical methods (Fernández *et al.* 2013).

However, in recent years, biological methods are also widely applied due to high environmental benefits. According to the report published by Danish technological institute, selection of suitable H<sub>2</sub>S removal technique varies for every biogas upgrading plant and also depends on the concentration of H<sub>2</sub>S permitted for end use. Additionally, two or more technologies can be used in conjunction to reach high H<sub>2</sub>S removal efficiency

When the H<sub>2</sub>S level in biogas is low, it is relatively more straightforward to remove within the digester. This is called in-situ desulphurization. However, there are also external desulphurization technologies available for treating both lower and high H<sub>2</sub>S concentration. In general, H<sub>2</sub>S removal methods are classified into two major groups based on the principle applied. Physio-chemical methods and biological methods. Physio-chemical methods can remove high concentration of H<sub>2</sub>S but can lead to various pollution problems such as emission of CO<sub>2</sub>, nitrogen oxides, and disposal of exhausted absorbents (Ramírez *et al.* 2011). On the other hand, biological methods have established as a mature technology with low operating cost and acquire high removal efficiency (>99 %). The technologies commonly employed for H<sub>2</sub>S removal are described in detail in the below sections.

### 2.5.1 Physio-chemical methods for H<sub>2</sub>S removal

The most common method engaged for H<sub>2</sub>S removal is by using absorbents such as activated carbon. It is a physical adsorption phenomenon where the surface pores hold pollutants through intermolecular forces. Activated carbon is useful when the pressure is increased to 8 bar and temperature of 50 to 70°C. The temperature can be achieved due to the heat produced onsite by biogas plants. Optimum moisture is required to carry out the process. Special coatings on activated carbon increase the adsorption of H<sub>2</sub>S. The coatings typically include, alkaline or oxide coatings, potassium iodide, and other coatings are also generally found in impregnated products. The capacity of sulfur removal is around 150 kg H<sub>2</sub>S/m<sup>3</sup>. Activated carbon suffer the drawback of disposal as they usually catch fire burns when left open after the exhaustion. The quantity of activated carbon increases with the concentration of H<sub>2</sub>S content. Usually, the carbon filling is adjusted to an operation time of 4,000 to 8,000 hours. Molecular sieves (zeolites) are another class of absorbents that compete with activated carbon.

Various journals have explored the use of H<sub>2</sub>S adsorbents in biogas upgrading (Bagreev *et al.* 2005); (Seredych and Bandosz, 2006); (Yan *et al.* 2004). The selectivity is very high as the polar compounds such as water, H<sub>2</sub>S, SO<sub>2</sub>, NH<sub>3</sub>, carbonyl sulfide, and mercaptans, are strongly absorbed, and non-polar compounds such as methane are not absorbed. However, compared to activated carbon, molecular sieves are expensive. Adsorption systems are used for flow rates between 10 – 10,000 m<sup>3</sup>/h (Truong and Abatzoglou, 2005). Alternatively, physical and chemical scrubbing methods are applied for H<sub>2</sub>S removal methods. Most of the scrubbing techniques employed for CO<sub>2</sub> removal such as water scrubbing, organic solvent scrubbing, etc. are

also used for H<sub>2</sub>S removal. The main disadvantage is the contaminated liquid stream that requires further cleaning methods. Advantage include high removal efficiency with no fluctuations (>99 %). Chemical scrubbing using iron-chelated process is economically viable with smallscale biogas systems (Demmink and Beenackers, 1998). It is also interesting that few chemicals such as Iron chlorides, ferric hydroxides, are directly added to the digester during anaerobic digestion to dissolve H<sub>2</sub>S content produced in the digester. Usually added in the form of liquids or solids, they react with hydrogen sulfide and produce insoluble iron sulfate salts which can be precipitated. H<sub>2</sub>S removal in chemical absorption lies within the stoichiometry whereas for physical adsorption it depends on the partial pressure of H<sub>2</sub>S (Horikawa *et al.* 2004). Thus, physical adsorption can absorb a more significant amount of H<sub>2</sub>S compared to chemical method.

This method is advantageous when a low concentration of H<sub>2</sub>S is present in the digester. However, it is not possible to attain high gas purity using this technology. Hence it is combined with other H<sub>2</sub>S removal technology to attain a high gas specification standard for biomethane.

### 2.5.2 Biological H<sub>2</sub>S removal

Biological H<sub>2</sub>S removal methods have proven advantageous in treating H<sub>2</sub>S from biogas. It is environmentally feasible and has low operational cost. Unlike physio-chemical methods, there are no secondary pollutants that are generated by biological methods. Various microorganisms have been tested and proven to be advantageous economically.

Table 2-7: Sulphur oxidizing bacteria and their energy sources

Bacterial species	Energy source	Electron acceptor	Process of removal	Reference
<i>Chlorobium limicola</i>	light	CO <sub>2</sub>	anaerobic	(Basu et al. 1994)
<i>Thiobacillus</i>	Sulfur	CO <sub>2</sub>	aerobic	(Alcántara, Velasco, and Revah, 2004)
<i>Acidithiobacillus thiooxidans</i>	Sulfur	CO <sub>2</sub>	aerobic	(Lee et al. 2006)
<i>Thiobacillus denitrificans</i>	Sulfur or disulfide	nitrate	aerobic	(Haaijer et al. 2006)
<i>Thiomicrospora sp.</i>	Carbon source	nitrate	anaerobic	(Gadekar, Nemati and Hill, 2006)
<i>Thiobacillus denitrificans</i>	Sulfur or disulphide	nitrate	anaerobic	(Cardinale et al. 2008)
<i>Acidithiobacillus ferrooxidans</i>	Sulfur	iron	aerobic	(Aroca et al., 2007)

These microorganisms have the sulfide-oxidizing ability and are commonly named as sulfur-oxidizing bacteria (SOB). Sorokin *et al.* (2016) studied the desulphurization effect of the sulfur-oxidizing bacterium and found bacterial strains such as *Thiobacillus ferroxidans*, *Thiobacillus thiooxidans*, *Thiobacillus thioparus*, *Sulfolobus acidocaldarius*, etc. that has the best H<sub>2</sub>S removal efficiency.

These microorganisms are attached in the form of biofilms and perform the H<sub>2</sub>S removal. There are three types of reactors used for biological treatment of H<sub>2</sub>S. They are biofilters, bio-trickling filters, and bio scrubbers.

All of the treatment technologies mentioned above use microorganisms to achieve H<sub>2</sub>S removal but differ in design, parameter, flexibility, operational parameters (Fernández *et al.* 2013). As such, biofiltration is widely applied due to favorable characteristics. This method has low operating cost and low energy requirements. The microorganisms are resistant to wide range of fluctuations and are easily adaptable (Ma *et al.* 2006). There are various factors considered in applying biofiltration technologies. Some of them are packing material, microbial diversity, nutrients supply, mode of operation (packed bed columns).

According to (Ryu, Kim and Cho, 2010) packing materials play a significant role in immobilizing bacteria. Thus, every packing material is selectively studied for the specific surface area, density, porosity, water holding capacity, etc. (Devinny, Deshusses, and Webster, 1999). Biofilters are packed bed columns. The packing is an organic material in which microorganisms are suspended. The most commonly used packing material include peat, compost, woodchips, etc (Wani, Branion, and Lau, 1998). The main disadvantage of the biofilters is acidification and accumulation of end products. This causes pH drop and the packing material to be replaced or washed from time to time. This replacement is avoided in biotrickling filters. Biotrickling filters, on the other hand, have better advantages as the packing material is inert and microorganisms adhere to the packing material and nutrients are in continuous recirculation within the packed column. This provides equal distribution of biomass and the produced intermediate products such as sulfur be removed in the recirculating nutrient solution.

There are various parameters for optimizing a biotrickling filter column that includes, elimination capacity and loading rate. Several commercial systems are available. The Biopuric process, developed in Germany, treats hydrogen sulfide concentration from ranging from 1,000 to 15,000 ppmv, and a single operation can remove as high as 200 kg H<sub>2</sub>S/d. Removal rates consistently range from 90 to 99 %. It is also important to mention that two classes of biological treatment are required to remove H<sub>2</sub>S. Aerobic and anoxic. There are also various other companies that have patented biofiltration technology for H<sub>2</sub>S removal such as BioSulfurex, from DMT environmental technology, Netherlands, Colsen B.V Bidox, system, EnviTec biogas, etc.

### 2.5.3 Sulfide oxidizing bacteria (SOB) and its application in H<sub>2</sub>S degradation

Various microorganisms have been explored for their degrading ability in H<sub>2</sub>S removal. The gaseous H<sub>2</sub>S is dissolved in the liquid to produce sulfide (HS<sup>-</sup>) which is biologically converted to elemental sulfur and sulfate by sulfur-oxidizing bacteria (SOB). The metabolic products as a result of H<sub>2</sub>S degradation by sulfur oxidizing bacteria such as sulfate can be easily removed due to the possible settlement of sulfur compounds. However, conversion from H<sub>2</sub>S to final metabolic products such as sulfate depends upon various parameters including, pH, temperature, and availability of oxygen. The biological conversion of H<sub>2</sub>S by sulfur-oxidizing bacteria is given in figure 2.6. The intermediate product, elemental sulfur produced as a result of incomplete oxidation of H<sub>2</sub>S to sulfate contributes to more enormous advantages in the industry due to nontoxic and noncorrosive nature. The elemental sulfur produced as sulfur globules on the outer cell membrane gets settled down at the bottom of the reactor which can be easily removed. Various microorganisms exhibit this function in various ways.

Majority of SOB is either phototrophic bacteria (green and purple) or chemotrophic bacteria (colorless sulfur bacteria). Table 2-7 describes various sulfur-oxidizing bacteria used in hydrogen sulfide removal. Phototrophic bacteria utilize a light source to reduce CO<sub>2</sub> to carbohydrates by using reduced sulfur compounds as an electron donor under anaerobic conditions. Chemotrophic bacteria chemically oxidize reduced sulfur compounds under aerobic conditions (i.e.) presence of oxygen. Figure 2.6 shows a simple example of sulfide oxidation by species *Thiobacillus*. Sulfide oxidation is carried out by a group of colorless chemoautotrophic bacteria. Most of them come under the genera, *Thiobacillus*, *Thiospira*, *Thiomicrospora*, *Thermothrix*, *Sulfolobus*, *Pseudomonas*, *Beggiatoa*. spp A dominant sulfide-oxidizing strain which exclusively produces elemental sulfur was isolated by (Visser and Antonie Van, 1997) which was named as *Thiobacillus* sp. W5. Vijay Kumar Gupta mentions that photographically produced sulfur globules have long sulfur chains whereas, chemotrophic bacteria produced sulfur rings. Such sulfur compounds could be used as fertilizer with economic profitability. Cork et al. (1983) proposed a microbial process for the treatment of H<sub>2</sub>S as an alternative to class process using the bacterial species *Chlorobium thiosulfatobium*.

There are various ways in which sulfur-oxidizing bacteria can remove H<sub>2</sub>S. Three essential ways as mentioned by (Pronk *et al.* 1990) include oxidation by oxygen using colorless sulfur bacteria, anaerobic oxidation by photosynthetic bacteria, and oxidation by denitrifying bacteria. All of the above ways have been utilized in engineering the SOB bacteria for the treatment of H<sub>2</sub>S gas in biogas streams. Two successful methods include scrubbing and biofiltration systems.

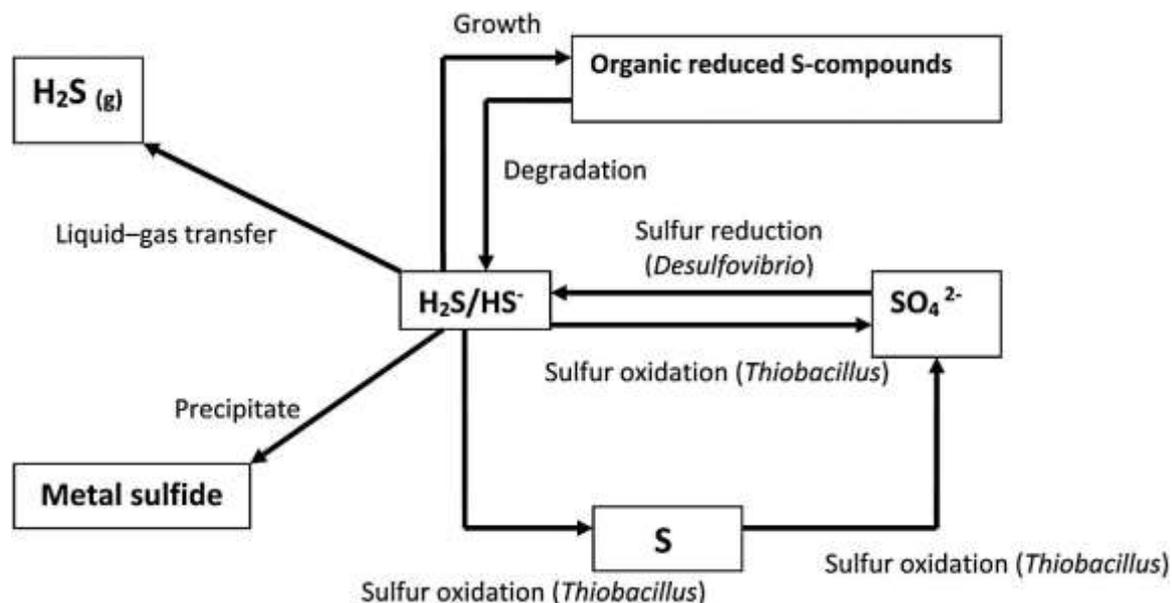


Figure 2.6: Biological sulfur oxidation cycle in  $\text{H}_2\text{S}$  degradation (Carrera *et al.* 2016)

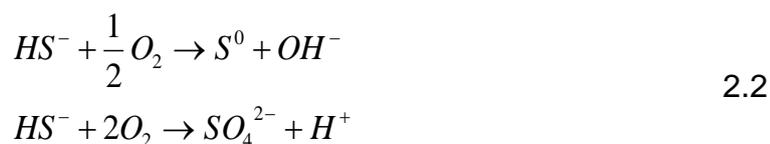
Bioscrubbers utilize liquid media for waste gas removal whereas biofilters utilize moist media. Both have been efficiently used for over 30 years according to Zhang *et al.* (2009). The use of applications depends on the need for removal and the demand required. For example, biofilters are preferred for treating more substantial quantities of contaminants such as in composting and in agricultural units. In every case, the biodegradation depends on the degree of solubility of a contaminant in water. Commonly, compounds with low molecular weight and high water solubilities such as  $\text{H}_2\text{S}$  and ammonia show better performance. Sulfur-oxidizing bacteria are more prone to changes in temperature and pH. Oxidation of  $\text{H}_2\text{S}$  makes the medium acidic due to the presence of sulfuric acid, and hence it is essential to add an external buffering agent for pH control. Biofilters and biotrickling filters both have moist, porous media for bacterial growth. When contaminant gases pass through filter media, the gases first get absorbed onto the solid surface of filter media and are absorbed into the moist biofilm, where bacteria react with the gases to undergo biodegradation. Biofilm, a combination of exopolymer and water, typically consist of 20 mm micrometer, facilitate the mass and oxygen transfer for pollutant degradation. Unlike traditional biotechnological approach and research works where biofilters and biotrickling filters are studied with pure cultures, practically industrial applications have mixed cultures of robust, thriving microorganisms. Biodegradation is thus caused by a mixture of bacteria, fungi in a complex ecosystem in a biotrickling filter. Hence, biotrickling filters are often nutrient limited. Initially inoculating with pollutant degrading microorganism is always required in case of biotrickling filters with inorganic packing material. However, over an extended period, only those organisms which have favorable conditions dominate the microbial

population in these filters. Thus, it is natural for a sulfur-oxidizing bacteria to live in a medium that contains an enormous amount of sulfur particles.

While biofilters rely on the indigenous bacteria present in the organic filter media, biotrickling filters employ highly robust inorganic plastic rings or polyurethane surfaces. These are called packing materials and have larger surface areas, hold nutrients and moisture long enough for bacterial biofilm formation and provide a structural appearance and longer life. Almost all recently developed biotrickling filters are supplied with inorganic packing materials. The recirculating medium consisting of nutrients for sulfur-oxidizing bacteria is recirculated continuously within the packing material to facilitate H<sub>2</sub>S degradation.

#### 2.5.4 Biotrickling filter and recent advances

Studies reveal that aerobic biotrickling filter could perform high H<sub>2</sub>S loading elimination (280 g S m<sup>-3</sup>h<sup>-1</sup>) under extreme conditions. They employ various microorganisms of the *Thiobacillus* genus (Macalady, Jones and Lyon, 2007) that effectively degrade H<sub>2</sub>S to elemental sulfur and sulfate as shown in Eq. (2).



As in all biological purification processes, the substance being cleansed in the trickling filter is biochemically converted to yield energy to the cell. The decrease of H<sub>2</sub>S concentration in the gas stream is usually at sufficient speed, particularly in seconds. Sublette and Sylvester, (1987b) showed that pure culture of *Thiobacillus* sp. could degrade H<sub>2</sub>S within 1-2s.

However, aerobic biotrickling filtration has suffered many criticisms due to the need for an additional supply of oxygen in the upgrading unit, which is dangerous and can cause dilution in biogas. However, concerning the climate change category (carbon dioxide (CO<sub>2</sub>) equivalent emission), aerobic desulphurization emits 5.24 kg CO<sub>2</sub> per hour while activated carbon desulphurization would emit 15.75 CO<sub>2</sub> per hour. Nevertheless, the overall environmental impact of biological techniques is much more favorable compared to other chemical and physicochemical techniques (Patricio Canto et al. 2016). Various species have already been successfully used in such biotrickling filters. Sercu et al (2005) utilized *Acidithiobacillus thiooxidans* spp for efficiently removing a concentration of 400 – 2,000 ppm of H<sub>2</sub>S. The high removal efficiency of 98 % was observed when Gabriel and Deschusses (2003) utilized *Thiobacillus* species for H<sub>2</sub>S removal. A biotrickling system with anaerobic sludge was developed by Soreanu et al (2005) for the removal of H<sub>2</sub>S from wastewater treatment plant. A two-stage H<sub>2</sub>S removal system was developed as a variation in the biotrickling filter by Pagella and De Feveri (2000) by

species *Thiobacillus ferrooxidans*. In General, most of the sulfur-oxidizing bacteria thrive under acidic pH between (2 - 3). Recent advances in biological desulphurization include simultaneous removal of ammonia and H<sub>2</sub>S by Tsang et al (2015) thereby achieving a removal efficiency of 98.5 % (H<sub>2</sub>S) and 99 % (NH<sub>3</sub>). Rolak et al (2016) identified a hyperthermophilic strain capable of degrading H<sub>2</sub>S and temperature (> 60 °C) and efficiently have been studied in the biotrickling filter. Xiang Tu et al (2016) explained the robustness of biotrickling filter operation under transient condition. Thus biotrickling filter is the most promising technology for H<sub>2</sub>S pollutant degradation and is more relevant in industrial biogas upgrading technologies.

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### **3 Biological aerobic desulphurization for the removal of hydrogen sulfide in biogas**

#### **3.1 Materials and methods**

All experiments at lab scale were carried out at the University of Duisburg-Essen. The experiments for hydrogen sulfide ( $\text{H}_2\text{S}$ ) removal were performed in a biotrickling filter as shown in figure 3.1. All gas flow measurements were made at standard temperature and pressure. The scheme of the experimental set up of the bio-trickling filter along with its technical specifications is described below.

##### **3.1.1 Biological aerobic desulphurization**

According to the guideline (VDI 3478, 2008), biological desulphurization is described as a process, based on the substance conversion of  $\text{H}_2\text{S}$  with the aid of biologically active microorganisms that form biofilms on biological trickling filters. They apply primarily to the decrease of  $\text{H}_2\text{S}$  that biodegrade at sufficient speed particularly in seconds.  $\text{H}_2\text{S}$  removal using biological desulphurization has always been aerobic, i.e., the  $\text{H}_2\text{S}$  is biologically oxidized into elemental sulfur and sulfate using aerobic microorganisms. Part 2 of guideline VDI 3478 (2008) defines the specifications necessary for the design and construction of bio-trickling filters.

##### **3.1.2 Design of biological trickling filter**

The scheme of experimental set up for the laboratory scale biotrickling filter is shown in figure 3.4. The principal design criteria for a biotrickling filter that includes contaminant loading rate, the volume of packing media, empty bed residence time, moisture content, temperature, pH and pressure drop across the bed are all detailed in the design specifications. The two primary tasks in engineering design of biotrickling filters such as sizing of the biotrickling filter and the engineering for the physical operating system is described in table 3-4. Sizing of the biotrickling filter depends on the volume of the packing media and the gas flow rate to attain the desired removal efficiency. Engineering of the physical operating system includes design and selection of equipment such as pipes and hoses, pumps, etc. The biotrickling filter was constructed using transparent plexiglass column (i.d. 250 mm, height 1600 mm). The column has a packed volume of 0.7 L. When deciding the size of the reactor, it is to be noted that the volume of the biotrickling bed and the height of the inflow area is accounted. The height varies according to throughput velocity and flow rate. Two sampling ports were distributed along the length of the column. It was designed according to Guideline VDI 3478 part 2 which states that a biotrickling filter should have a minimum of 0.5 m between the inflow and outflow areas as the distance of separation.

Parameters considered for the given biotrickling filter according to guideline VDI 3478 part 2 are shown in table 3-1.

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Table 3-1: Design of trickle bed reactor according to guideline VDI 3478 part 2

Parameter	Unit	Current design
Clean gas concentration	mg/m <sup>3</sup>	<10
Raw gas concentration	g/m <sup>3</sup>	1,000
The height of carrier material h Column ratio h:d	M	0.6 m >3:1
Pressure loss	Pa/m	
Gas flow rate Q	m <sup>3</sup> /h	0.02 - 0.08
Retention time	S	12s - 150s
The volume of trickle bed	m <sup>3</sup>	0.0007

The synthetic pollutant gas stream containing H<sub>2</sub>S (0.1 vol %, balance N<sub>2</sub>) was supplied to the biotrickling filter from compressed gas cylinder obtained from Linde Gas AG, Düsseldorf (Germany).

Packing material (Figure 3.2) made up of plastic saddle ring (Okkerse *et al.*, 1999) was initially used to fill the filter bed and to facilitate the microorganisms to be able to adhere firmly to the column.

It is speculated that the high pollutant mass transfer is possible with polyurethane or plastic rings are used in combination with nutrient recirculation. Plastic rings serve as a synthetic inert carrier material in many biotrickling filters and also has various advantages over organic carrier materials.

Although inert carrier material such as plastic rings may be expensive than natural ones, high lifetime and long performance can nullify high investment cost (Jin, Veiga, and Kennes, 2005). These plastic rings are characterized by high physical strength, lightweight, chemically inert, and do not suffer biodegradation or bed compaction.

The bio-trickling filter column was randomly packed with plastic rings to have better air and liquid distribution along the filter bed. Thus the void fraction of the plastic ring exceeded 90 %. Its low density allowed less bed compaction. Typical characteristics of the plastic rings used for this experimental set up are described in table 3-2. The column of the reactor was housed in a liquid reservoir attached to the bottom using a screw clamp. This ensured that the column could be detached easily for replacement in case of damage or sampling. Two additional pressure ports connected to manometer were also installed at the top and bottom of the column to measure the pressure drop. The advantage of using plastic rings also ensured that there is no bed compaction and

minimal pressure drop. The gas flow was upwards as in countercurrent mode with the recirculating liquid.

The packing material (plastic rings) was randomly packed and supported by sieve plate at the bottom of the column to ensure a homogenous distribution of inlet pollutant gas stream across the packed bed column. Apart from carbon and pH, microorganisms require other components such as nitrogen, phosphorus, and various trace elements.



Figure 3.1: Biotrickling filter designed and constructed at the University Duisburg Essen. From left: Picture 1 (left side) shows the fabricated biotrickling filter with the liquid reservoir. Picture 2 (right side) shows the column for gas flow (Rajavelu 2015).

Table 3-2: Characteristics of plastic rings used for H<sub>2</sub>S removal in the biotrickling filter

Packing	Void fraction*	Specific surface area (x 10 m <sup>-1</sup> )	Density* (g/cm <sup>3</sup> )	Biofilm formation (days)	Preferred temperature (°C)	Lifetime (years)
Plastic rings	90 -95	20 - 24	0.06 – 0.08	5 -15	< 65	>10

\*Oriental values obtained from the purchased company

It was supplied through a nutrient medium which trickled and recirculated along the filter bed. The composition of the nutrient medium is given in table 3-3. The trickling medium containing the nutrient solution was kept at room temperature throughout the process. According to VDI guideline, for loose and structured packing as carrier materials, the

trickle density must be less than  $5 \text{ m}^3/(\text{m}^3 \cdot \text{h})$ . This ensures that the biofilm is not washed off during the process from the carrier surface by shear forces. Trickling liquid containing nutrient medium was recirculated continuously at a flow rate of 255 ml/min using a peristaltic pump.



Figure 3.2: Plastic saddle rings used as a packing material to fill the column of biotrickling filter (Rajavelu 2015).

Table 3-3: Composition of nutrient solution used for the growth of Sulphur oxidizing bacteria in the biotrickling filter

Reagent	Concentration (g/L)	Percentage (%)
Total Nitrogen (N)	95	8
Ammonium nitrogen		1.7
Nitrate		0.7
Urea		5.6
Water soluble phosphate ( $\text{P}_2\text{O}_5$ )	95	8
Water soluble potassium ( $\text{K}_2\text{O}$ )	75	6
Trace elements (B, Cu, Mn, Zn)*		0.01,0.005,0.01,0.01
pH 7.1		

\*Chelate of EDTA

Minimum trickle density (VDI 3478 part 1, 2011) of  $0.01 \text{ m}^3/(\text{m}^2 \cdot \text{h})$  was maintained to ensure a wetted surface area which was essential for sufficient biological oxidation. The trickling nutrient medium was also aerated using oxygen bubbler using a peristaltic pump to ensure that the bacteria have sufficient aeration required for desulphurization. Depending on the quantity of the pollutants such as dust and salt, it may be necessary for certain circumstances to increase the biomass removal rate.



Figure 3.3: Image of the physical operation system and engineering design constructed at lab scale for the biotrickling filter operation for  $\text{H}_2\text{S}$  removal (Rajavelu 2015).

Usually its 0.02 % to 0.05 % (VDI 3478 part 2, 2011). Conditioning of trickling medium is done periodically to replace consumed medium with fresh water and for mixing new nutrient concentrate. Time after time, the trickling medium was mixed with the nutrient source, and later fresh water is mixed in and the pH was checked. Inorganic carbon source was supplied as  $\text{NaHCO}_3$  ( $3 \text{ g C}\cdot\text{L}^{-1}$ ) separately by a peristaltic pump (its-dos master from iks aquastar GmbH, (Germany) near the aeration unit. Since the process was studied as acidic biofiltration, the pH was maintained at 2.0 in the bio trickling filter by adding  $\text{NaOH}$  ( $1 \text{ mol}\cdot\text{L}^{-1}$ ) and  $\text{HCl}$  ( $1 \text{ mol}\cdot\text{L}^{-1}$ ). The pH, temperature, dissolved oxygen, and redox potential are measured and controlled automatically using programmed iks aquastar industrial software from iks aquastar HD, (Germany). In this case, all piping for gas supply was made from Teflon tubing model (PFAN - CRQS) with DIN standard 73378 purchased from company Festo GmbH (Germany). For recirculating liquid, silicone rubber polyamide pipes were used.

The junctions were connected using plastic valves for liquid. For gas, corrosive resistant gas valves model types (PVDF - CRQST) from Festo GmbH, (Germany) were used.  $H_2S$  concentration was measured at the outlet and the inlet of the bed by an online electrochemical sensor (Transmitter Sens  $H_2S$ -3,000-EC).

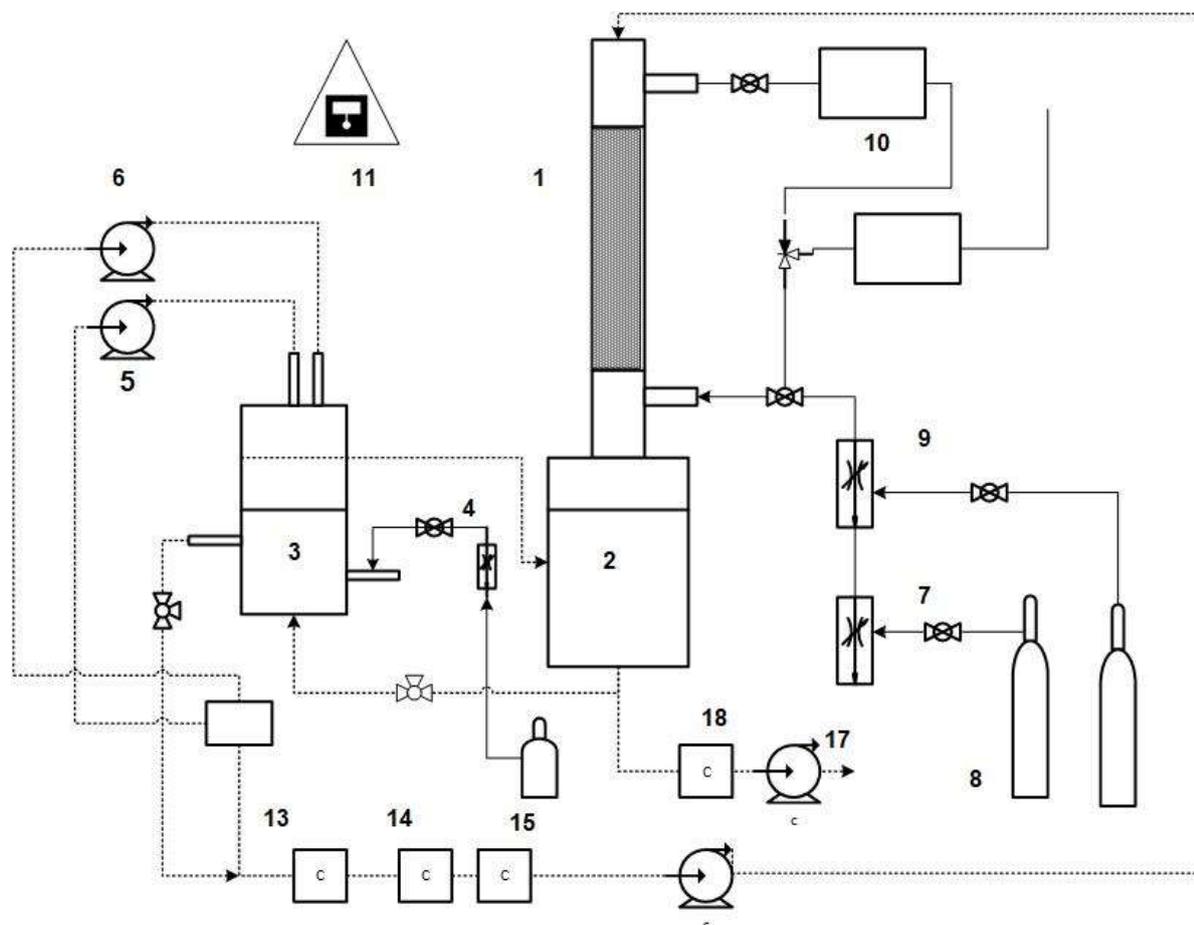


Figure 3.4: Process layout of the engineering design constructed for biotrickling filter operation. Dotted lines represent the liquid flow.

It was connected to a computer for continuous data collection using a control unit purchased from company ExTox GmbH, Unna (Germany).

Table 3-4: Technical specifications of the biotrickling filter system. Descriptions of components found in figure 3.4.

	<b>Main reactor</b>	<b>Aeration unit</b>	<b>Gas phase inlet</b>	<b>Gas phase outlet</b>	<b>Liquid phase recirculation</b>
Equipment	1.Main reactor 2.liquid reservoir	3.Aerator 4.Air inlet pump 5.NaOH pump 6.HCL pump	7.H <sub>2</sub> S DMFC 8.H <sub>2</sub> S cylinder 9.N <sub>2</sub> DMFC	10.Gas analyzer 11.H <sub>2</sub> S alarm system	12.Recirculation pump 13.pH electrode 14. ORP electrode 15.Control panel
Type/ model	1.Vertical cylindrical 2.Vertical, cylindrical	3.vertical, cylindrical 4.vacuum pump 5.peristaltic pump 6.Peristaltic pump	7. low p flow, IP40 8. Gas cylinder 9. DFC 4600	10.ET8DA 11.ET8DA	12.Peristaltic 13.Glass electrode 14.Glass electrode 15.Industrial control panel
Manufacturer	1.Self-made 2.Self-made	3.Self made reactor 5.iks vario blue 6. iks vario blue	7. Bronkhorst 8. Linde 9. Dielen	10. ExTox GmbH 11. ExTox GmbH	12. iks aquastar 13. iks aquastar 14,15,16. iks aquastar
Main construction material	1.PVC 2.PVC	3.PVC 4. PP 5. PVC 6. PVC	7.316 SS, Viton 8. SS 316 9. 416 SS, Viton	10, 11.steel, powdered and coated textured in RAL -7035	12. PVC 13. glass 14.glass 16. black polysulfone

Main dimensions	1. D = 6 cm, H = 55 V useful = 0.7 L 2. D = 16 cm H = 12 V useful = 1-2 L	3. D = 8 cm, H = 25 cm, V = 1 L 5. 50*60*82 mm 6. 50*60*82 mm	7. 77*111*25 mm 8. D 140 mm V 10. L 9. 77*111*25 mm	10.760 mm*600 mm* 350 mm	12.120 mm * 12 mm 13.120 mm * 12 mm 15.Wall thickness 16 16.120 mm * 12 mm
Other specifications	1.Gas port H: 2 cm Packing : plastic rings Rings size = 1*1*1 mm Specific surface area = 600 m.m <sup>3</sup> Liquid hold up = 98 % High	2.Fine diffuser (ceramic) 4.Q max = 1 L/min 5.on/off control (Q max =240 VAC, 20 rpm, 50 Hz) 6. On/off control (Q max = 40 VAC, 20 rpm, 50 Hz)	7.Q max for H <sub>2</sub> S 100 L/h In/out pressure 1/0 bar V; m <sup>3</sup> , P bar 9. Q max for N <sub>2</sub> = 2,000 ml/min	10. Range of flow : 0-3,000 ppmv of H <sub>2</sub> S	
Monitored parameters	1.Pressure drop (M) 2.Liquid Level (M)	2.Liquid level (A) 7.Q Air in ( A) 5.Base(A) 6.Acid(A)	Q H <sub>2</sub> S ( A) Pressure (M) Q N <sub>2</sub> (A)	10. H <sub>2</sub> S , CH <sub>4</sub> , CO <sub>2</sub> , O <sub>2</sub> ,	12. Q recirculation(M)
Operational range	Optimum mass flow in terms of LR H <sub>2</sub> S =14.586 g pollutant .m <sup>-3</sup> .h <sup>-1</sup> ) EBRT = 16s - 250s V = 0.7 L	Q air <sub>in</sub> = 250 ml.min <sup>-1</sup>	H <sub>2</sub> S = 0.1 vol %		TLV = 3 l/h PH = 1.5-3

Monitored paramters = M (manuel) A = (Automated)

LR = Loading rate

EBRT = empty bed residence time

TLV = trickling liquid velocity

DMFC = Differential mass flow controllers

## 3.2 Analytical methods

### 3.2.1 Gas Sampling

Gas sampling measurements were made under a normal temperature condition in the range of 20 - 30 °C. A single ET-8DA gas analyzer obtained from company ExTox GmbH (Germany) was used to measure the H<sub>2</sub>S gas samples from the inlet and the outlet port. The gas analyzer was customized for H<sub>2</sub>S measurements. It consisted of two specific electrochemical H<sub>2</sub>S sensors namely transmitter Sensor 1 which is named as H<sub>2</sub>S-100-EC-BIO for measuring H<sub>2</sub>S concentration at 0-100 ppm<sub>v</sub>, the accuracy of +/- 1 % and transmitter Sensor 2 named as H<sub>2</sub>S-3,000-EC for measuring H<sub>2</sub>S concentration at 0-3,000 ppm<sub>v</sub> with an accuracy of +/- 5 %. The gas analyzer also consisted of an infrared sensor for gases such as CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, respectively. The sensors were fitted externally to the rear exit of biotrickling filter for handiness in measurement. Figure 3.5 shows the technical layout of sensors.

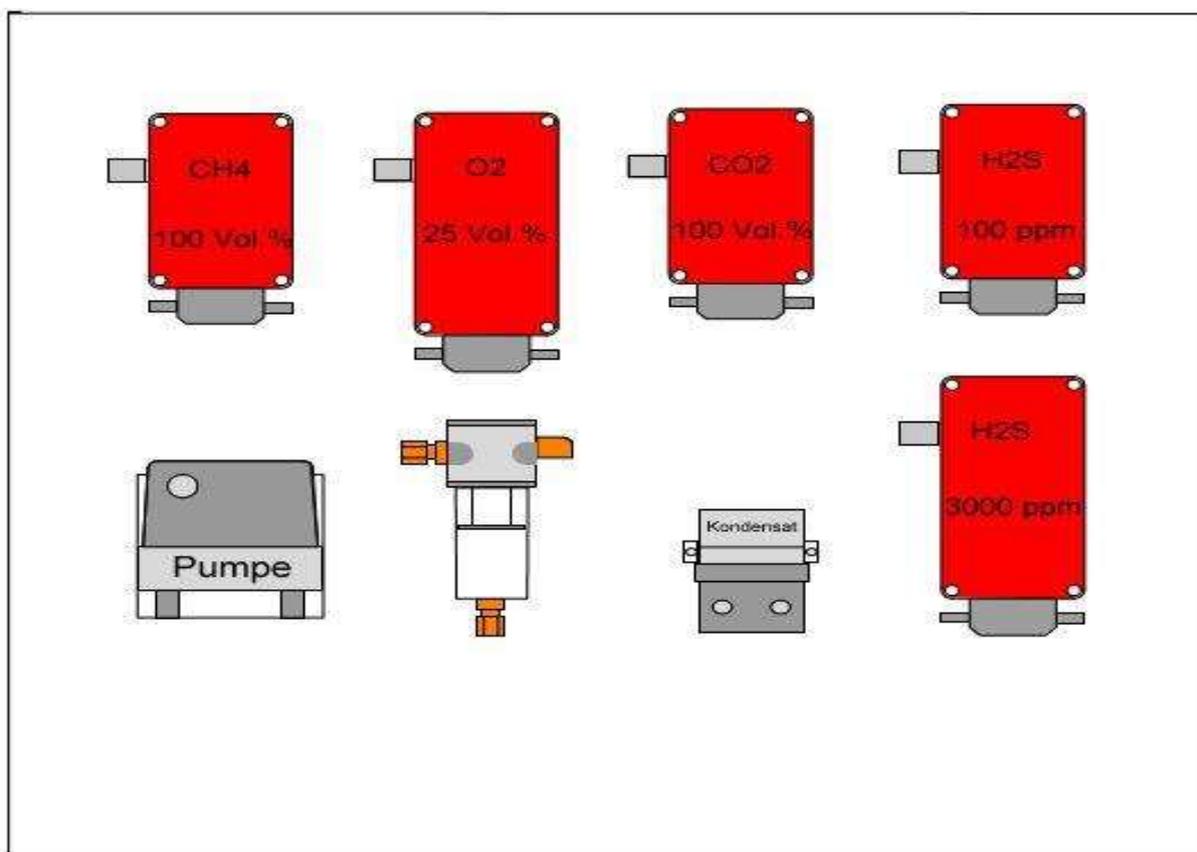


Figure 3.5: Technical layout of sensors used for gas analysis for H<sub>2</sub>S removal

Measurement points for point sources are subject to requirements of guidelines from VDI 2066 part 1 and VDI 4200. The technical specification of the H<sub>2</sub>S sensor is given in

table 3-5. The sensors are programmed for measurement at the gas outlet port for every 3 seconds. Figure 3.6 shows the direction of gas flow into the sensors from the biotrickling filter to other components of the gas analyzer system.

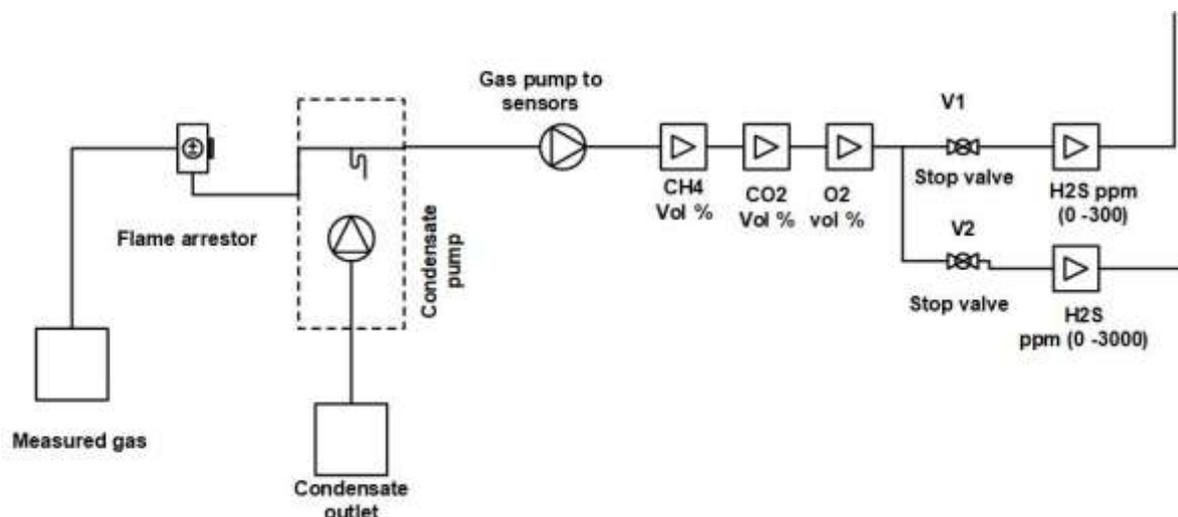


Figure 3.6: Diagram describing the passage of gas flow from the biotrickling filter to the gas sensors for analysis

Other components such as flame arrestors and condensate trap were also installed adjacent to the online external sensors to ensure safety and superior measurement accuracy as shown in figure 3.5. The gas at the exit of biotrickling filter first passes through the flame arrestor, condensate pump, condensate trap and then to the sensors and finally to the caustic trap before it exits into the atmosphere through exhaust during experimental trials. For calibration purpose, the sensors are always flushed with  $N_2$  before the desired gas concentration is passed through. The data is automatically registered using computer software called Terminal.exe file for every 3 seconds. The signal from the transmitters is communicated to laptops using RS 232 via Profibus and Modbus connections. The measured data for gases is thus stored in PC using ExTox Data Logger ET-SL file.

Table 3-5: Technical specification  $H_2S$  sensor

Principle	Unit	Electrochemical
Measuring range	ppm <sub>v</sub> of $H_2S$	Sensor 1 $H_2S$ 100 (0-100) Sensor 2 $H_2S$ 3,000 (0-3,000)
Output signal	mA	4 – 20
Temperature range	°C	-20 to +40°C
Response time $t_{90}$	s	> 3

### 3.2.2 Liquid Sampling

Liquid sampling for H<sub>2</sub>S removal was always taken from recirculation point of the bio trickling filter. The liquid was drawn off from the purge valve and immediately analyzed for sulfate concentration. It was stored below 6 °C (43 °F) up to 28 days before measurement. The frequency of sampling was for every 20 minutes. The liquid samples were mainly analyzed for sulfate concentration [S-SO<sub>4</sub><sup>2-</sup>].

The sulfate content was used as an indicator to ensure that biological oxidation had taken place. The concentration of sulfate was determined in the liquid medium using standard turbidometric method (APHA, 1999) using SulfaVer® 4 Sulfate Reagent kit purchased from Hach Lange company (Germany). The testing method was based on ISO 8466-1 and DIN 38402 A51 standards.

The measurement mainly uses turbidometric barium method to identify sulfate content in the sample. The method was accepted from Standard Methods for Examination of Water and Wastewater.

SulfaVer® 4 Sulfate Reagent kit (Method 8501) included:

- SulfaVer® 4 Reagent sample cells
- Barium chloride powder

The following procedure was adopted for the measurement of sulfate content in the sample

1. A predetermined amount of recirculating liquid was collected from the bio trickling filter
2. A pinch of barium chloride is added to the sample and shaken well. Formation of white precipitate shows the presence of sulfate.
3. The concentration of the sulfate present in the precipitated solution can be measured using Hach Lange Instrument DR 2800. The program was always set for sulfate 680 nm for measurement and reading.

For technical and biological reasons, a pH in the neutral range is optimal in many cases for the trickling liquid and biofilm according to the guideline VDI 3478. However, due to the best activity of acidophilic microorganisms in H<sub>2</sub>S removal, the pH was maintained acidic (pH = 2) and was measured continuously and controlled (DIN 38404-5).

By monitoring dissolved oxygen (DO) concentration in the liquid phase, the conclusion can be obtained on the quantity of aeration required for microorganisms.

### 3.2.3 Microorganism source and biomass immobilization

The microbial inoculum used in bio trickling filter of H<sub>2</sub>S removal was obtained from desulphurization plant (bio trickling filter) installed at the “bioenergy GmbH” biogas plant, located in Lünen NRW Germany.

The full-scale biogas plant produces 9 million cubic meters of biogas per annum, and that generates 27 million kWh of electricity after desulphurization. The inoculum was directly collected from the recirculating tower of the desulphurization plant located next to CO<sub>2</sub> scrubbing unit. The inoculum had an extremely low pH value (pH=3) with a very high sulfate content of 2.3 g [SO<sub>4</sub><sup>2-</sup>-S].

To build an initial microbial community in the biotrickling filter, the inoculum containing sulfur-oxidizing bacteria was introduced into the packed column containing carrier material for biofilm formation. Such seeding method is referred to as bioaugmentation (Kennes and Thalasso, 1998).

The bioaugmentation process or biomass immobilization in the packed column for this method was adopted from Ramírez *et al.* (2009) as follows.

1. The microbial inoculum containing the sulfur-oxidizing bacteria was loaded into the biotrickling filter.
2. The volume of inoculum loaded was 2 L, and it was recirculated continuously along the packed column with the carrier material (plastic rings) using the peristaltic pump at a constant flow rate of around 180 ml·min<sup>-1</sup>
3. The inoculum was recirculated, and the pH, temperature, sulfate concentration and biomass in suspension were continuously monitored.
4. When the sulfate concentration falls below 1.0 g/L, half (50 % v/v) of the recirculated volume is drawn off and replaced with fresh medium.
5. After two weeks, inoculation, aeration was supplied by mean of oxygen diffuser into the bio trickling filter. Step 4 is repeated every two days, and the successive cycles were performed until visible biomass layer could be observed.

Operating conditions of the bio trickling filter and the dominant environmental factors affect the development of specific microbial community (Langenhove *et al.* 1992).

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Often, such a high sulfate content  $> 2.3 \text{ g } [\text{S-SO}_4^{2-}]$  in the microbial inoculum indicates the presence of sulfur-oxidizing bacterial community that is capable of degrading  $\text{H}_2\text{S}$  content in biogas. Thus the presence of a dense culture of SOB biofilm ideal for  $\text{H}_2\text{S}$  gas treatment can be inferred

### 3.2.4 Fluorescent in situ hybridization (FISH)

The dominant sulfur-oxidizing bacteria (SOB) present in the column and the recirculating liquid was identified using Fluorescent In Situ Hybridization Technique (FISH). Most of the sulfur-oxidizing bacteria fall within the group of proteobacteria (alpha, Beta and gamma) which was exploited using FISH identification.

Fluorescently labeled probes THIO1 and ALF 968 targeting the *Acidithiobacillus* spp genus and the related alphaproteobacterial species was used to confirm and identify the targeted sulfide-oxidizing bacteria.

For FISH analysis, the samples were prepared using the following steps

1. 5 ml of fresh sludge samples obtained from biogas plant were immediately fixed in ethanol solution and stored at  $-20 \text{ }^\circ\text{C}$  before further analysis.
2. The fixed samples were vibrated in Mixer mill MM2000 from Restch Company (Germany) which allows the bacterial biomass clustered in sulfur crystals present in the sludge sample could be separated.
3. After 15 minutes, 1 ml of the mixture is transferred to 2 ml centrifuge tubes.
4. The mixture is then diluted with distilled water in 1:2 ratio in centrifuge tubes and centrifuged at a speed of  $1,000 \times g$  for 15 minutes to separate the biomass from excess sulfur particles
5. The supernatant obtained from initial centrifugation is again transferred to another 2 ml tubes for further centrifugation at  $2,000 \times g$  for 15 minutes.
6. step 5 is repeated for 2 - 3 times, the final mixture is ready for FISH analysis.

FISH and DAPI (4'6 diamido-2-phenylindole) ( $5 \mu\text{g ml}^{-1}$ ) staining were performed as described previously (Pernthaler *et al.*, 2001). The sequence of 16S rRNA oligonucleotide probes used and the Percentage of formamide used in hybridization buffer is given in table 3-6.

DSMZ Braunschweig, (Germany) provided all the probes used for the purpose. The samples were observed under phase-contrast and epifluorescence on a Zeiss

Oberkochen company (Germany) AXIOPlan Imager M1 compound light microscope with AxioVision v4.4 capture software.

Table 3-6: FISH probes used in the experiment

Probe	Specificity	Sequence	Formamide	Target	Reference
ALF 968	Alpha - group	GGTAAGGTTCTGCGCGTT	35	16S	Neef <i>et al.</i> (1997)
EUB 338	Most bacteria	GCTGCCTCCCGTAGGAGT	0 - 35	16S	Amann <i>et al.</i> (1990)
THIO1	<i>Acidithiobacillus</i> spp	GCGCTTTCTGGGGTCTGC	35	16S	González-Toril <i>et al.</i> (2003)

### 3.2.5 Biotrickling filter performance calculations

The effect of suspended sulfur-oxidizing bacteria in a biofilm on biodegradation has to be estimated in each experimental trial. The process related principles of biodegradation with the aid of suspended microorganisms are presented in guideline VDI 3478 Part 1. Operation of the biotrickling filter is characterized by Loading Rate (LR) or maximum degradation rate for which the reactor has to be designed.

According to the guideline of VDI 3478 Part 2, volumetric loading rate is expressed as flow rate/reactor volume in  $\text{m}^3/(\text{m}^3 \cdot \text{h})$  or Mass flow/reactor volume in  $\text{g}/(\text{m}^3 \cdot \text{h})$ . In contrast, the degradation rate is given about the water free dry matter (DM) of the microorganisms (equivalence procedure): mass flow/microorganism mass in expressed in  $\text{g}/(\text{h} \cdot \text{g}_{\text{DM}})$ . The mass loading rate or loading rate as in referred here is the amount of pollutant that is introduced into the biotrickling filter per unit volume of the bed. The equation of loading rate denoted as loading rate (LR) is given in equation 3.2. Pollutant concentrations are usually denoted as mass per volume. Thus conversion of volumetric to gas concentrations are done using ideal gas laws (Jin, Veiga, and Kennes, 2005)

$$\text{EBRT} = V / (Q_{\text{biogas}} + Q_{\text{Air in}}) \quad 3.1$$

EBRT	Empty bed residence time	S
V	Reactor bed volume	$\text{m}^3$
$Q_{\text{biogas}} + Q_{\text{Air in}}$	The total gas flow rate	$\text{g pollutant} \cdot \text{m}^{-3}$

in

Another significant design parameter for bio trickling filter is the contact time or Empty bed residence time (EBRT) as described in the equation in 3.1. This is the average time a particular volume of air stays inside the system. For a given flow, a minimum residence time decides the size of the reactor bed and hence is crucial for the cost in designing the system (Jördening and Winter, 2005).

It should be noted that elimination capacity, EBRT and loading rate are calculated using the volume of actual packed bed mass and not the volume of the whole reactor. The actual gas residence time is always lower due to the packing characteristics.

$$LR = [(Q_{\text{biogas}} + Q_{\text{air in}} * C_{\text{in}}) / V] \quad 3.2$$

LR	Loading Rate	$\text{g pollutant} \cdot \text{m}^{-3} \cdot \text{h}^{-1}$
$Q_{\text{biogas}} + Q_{\text{air in}}$	The total gas flow rate	
$C_{\text{in}}$	Pollutant inlet concentration	$\text{g pollutant} \cdot \text{m}^{-3}$
V	Reactor bed volume	$\text{m}^3$

Since the actual porosity is hard to measure, empty bed retention time or EBRT is measured using the volume of the bed. EBRT represents the time the gas is in contact with the packed bed. It is also known as gas contact time, i.e., the mass transfer time between the waste gas and the contact surface of the biofilm and its a matter of seconds (VDI 3478 part 2). Depending on the composition and concentration of air pollutant, it has to be decided whether a single or multi-stage absorption plant is required. (VDI 3478 part 2). To satisfy the requirements of TA Luft act (Technical Instructions on Clean Air), the gas contact time for readily soluble and readily degradable compounds ranges from 5 s to 20 s, whereas significantly longer for poorly soluble and poorly degradable compounds depending on input concentration.

$$RE = [(C_{\text{in}} - C_{\text{out}}) / C_{\text{in}}] * 100 \quad 3.3$$

RE	Removal efficiency	
V	Reactor bed volume	$\text{m}^3$
$C_{\text{in}}$	pollutant inlet concentration	$\text{g pollutant} \cdot \text{m}^{-3}$
$C_{\text{out}}$	pollutant outlet concentration	$\text{g pollutant} \cdot \text{m}^{-3}$

The Removal efficiency (RE) is given as percentage. It is also known as separation efficiency according to VDI 3478 Part 1 and represents the fraction (%) of the

contaminant removed. It is the characteristic of each reactor as it varies with the concentration of the pollutant and is not referred to the reactor size or the bed volume. Removal efficiency is defined in equation 3.3

$$EC = [(Q_{\text{biogas}} + Q_{\text{Air in}}) * [(C_{\text{in}} - C_{\text{out}})] / V \quad 3.4$$

EC	Elimination capacity	$\text{g pollutant} \cdot \text{m}^{-3} \cdot \text{h}^{-1}$
V	Reactor bed volume	$\text{m}^3$
$Q_{\text{biogas}} + Q_{\text{air in}}$	Total gas flow rate	$\text{g pollutant} \cdot \text{m}^{-3}$
$C_{\text{in}}$	pollutant inlet concentration	$\text{g pollutant} \cdot \text{m}^{-3}$
$C_{\text{out}}$	pollutant outlet concentration	$\text{g pollutant} \cdot \text{m}^{-3}$

Amongst the various design parameters mentioned above, only four are independent parameters such as reactor height, the gas concentration at the inlet and outlet and volumetric flow rate. Other variables are majorly interdependent.

The Elimination capacity (EC) as given in equation 3.4 represents the mass of contaminant eliminated per unit volume of the reactor per unit time. When the reactor performs with 100 % RE, the EC is equal to RE. The specific elimination capacity EC and thus the performance of the reactor depends on the input of concentration  $C_{\text{in}}$ , water solubility and biodegradation rate of compounds (VDI 3478 Part 2).

### 3.3 Results and discussion

#### 3.3.1 Startup operation and performance of H<sub>2</sub>S bio trickling filter

As biological desulphurization has been successfully established in biogas cleaning technologies, there is also a constant interest in stabilizing the technology towards the end-user application. To reduce the H<sub>2</sub>S concentration in biogas and efficiently operate the system, a better understanding of the operational parameters of the existing system is necessary.

The technical feasibility of using a bio trickling filter operated at lab scale for the treatment of H<sub>2</sub>S gas was studied by Fortuny *et al.* (2008) who showed a complicated relationship between the given reactor loading capacity and its removal efficiency. Also, preliminary results of system robustness with short-term perturbations and packing material was studied by Bugu and Labat, (2013).

A similar study was conducted to understand the performance of constructed bio trickling filter and its removal efficiency concerning its given loading rate. Also, the effect

of gas contact time, Empty bed residence Time (EBRT), and oxygen supply was studied in detail to know the extremities in the reactor performance. This, in turn, led to the optimizing of start phase with improved reactor design.

The work presented in this chapter aims to study the start-up period and initial operational optimization of H<sub>2</sub>S bio trickling filter. The startup phase was studied with an inlet concentration of H<sub>2</sub>S of 1,000 ppm with the loading rate of 14.285 g of H<sub>2</sub>S m<sup>-3</sup>·h<sup>-1</sup>.

The variations in EBRT, gas contact time and oxygen supply was studied concerning the reactor performance such as elimination capacity and removal efficiency. Also, discontinuous oxygen supply showed significant variations with the H<sub>2</sub>S removal which is detailed below.

### 3.3.2 Inoculum and startup

Bio trickling filter was initially inoculated with oxidizing sulfur biomass to speed up the startup period. It was diluted in 1:1 ratio with Millipore water thus having final volatile suspended solids (VSS) of 1.0 g L<sup>-1</sup>. It is common to maintain VSS of 1.9 - 2 g L<sup>-1</sup> to ensure free liquid trickling along the bioreactor. The bacterial inoculum was recirculated initially for 24 hrs without any gas supply. Then the gas was fed into the bio trickling filter at a constant loading rate of 14.285 g of H<sub>2</sub>S m<sup>-3</sup>·h<sup>-1</sup> with the concentration of 1,000 ppm. Since the initial pH of the bacterial inoculum was 3, the pH control system ensured that the pH was maintained for the better activity of the sulfur-oxidizing bacteria. The aeration of the recirculating liquid was continuously done so that the bacteria have enough oxygen for oxidation of H<sub>2</sub>S. Inorganic carbonate was supplied separately into the recirculating liquid to avoid carbon limitation. During the first few days, the liquid was not replenished, but the pH was noted continuously for lowering to less than 1.8, then the new mineral medium was supplied.

### 3.3.3 Experimental conditions

During the initial start-up period, the following experiments were performed to study the gas contact time and reactor performance. The initial inlet load of H<sub>2</sub>S concentration was given continuously for 15 days without any fluctuations, and later the load was slowly increased. The inlet load is defined as the mass (g) of gas pollutant loaded per volume (m<sup>3</sup>) of filter bed per hour. As shown in Table 3-7, the EBRT was reduced stepwise from 250 s to 43 s through an increase in gas flow rates at a constant H<sub>2</sub>S concentration of 1,000 ppm. Each EBRT was kept for 1.5 h.

Also, the hydraulic retention time (HRT) of 12 h was determined. The trickling velocity 180 ml·min<sup>-1</sup> was maintained constant throughout the experiment. To test the effect of dissolved oxygen supply in the process, experimental trials were made with discontinuous oxygen after the initial operation.

Table 3-7: Experimental conditions at the startup phase

Experiment	[H <sub>2</sub> S] ppm	[H <sub>2</sub> S] LR (g S-H <sub>2</sub> S m <sup>-3</sup> ·h <sup>-1</sup> )	EBRT (s)
1	1,000	14.285	250
2	1,000	28.571	126
3	1,000	57.428	62
4	1,000	85.713	43

LR = Loading rate of H<sub>2</sub>S gas; EBRT = Empty bed residence time;

After inoculation and startup, less than in one hr, elimination of H<sub>2</sub>S occurred, and the removal efficiency gradually increased and reached to the maximum of 99 % as it was recorded in the H<sub>2</sub>S Sensor from Extox gas analyzer. Unlike the progressive increase in Removal Efficiency (RE) after two days (Montebello *et al.*, 2010), the RE was quite earlier in this system. This is due to the immediate inoculation of bacteria directly obtained from desulphurization tower from the biogas plant. Thus the bacterial community is already acclimatized, and hence the startup of the system was earlier. The RE remained constant through the 15-day operation. After 15 days of operation, the loading rate was slowly increased. The biofilm developed on the surface of plastic rings during the 15-day operation. The thin yellowish slimy layer was observed inside the wall of the column (data not shown).

### 3.3.4 Effect of loading rate and empty bed residence time (EBRT) on H<sub>2</sub>S removal

The effect of loading rate was studied by varying the gas contact time or empty bed residence time (EBRT) for experiments 1 to 4. By maintaining a constant inlet concentration, the EBRT was reduced from 250 s to 43 s. Thus, the loading rate expressed in g S - H<sub>2</sub>S m<sup>-3</sup>· h<sup>-1</sup> kept increasing when the EBRT was decreased. Each EBRT was kept for 1.5 h, and the variations were studied. As shown in the figure 3.7 the removal efficiency (RE) was 99 % when EBRT was at 250 s. The corresponding loading rate was 14.285 g S- H<sub>2</sub>S m<sup>-3</sup>· h<sup>-1</sup>. A decrease in removal efficiency was observed when the EBRT was decreased slowly from 250 s to 43 s as shown in figure 3.7. Eventually, the removal efficiency was reduced to 95 % when the corresponding loading rate was found to be 85.713 g S - H<sub>2</sub>S m<sup>-3</sup>·h<sup>-1</sup>. It is noted that though the inlet loading rate was increased 6.0 times higher from 14.285 to 85.713 g S - H<sub>2</sub>S m<sup>-3</sup> the decrease in RE was only from 99 % to 95 %. This decrease in removal efficiency can be attributed to the fact that the system favored a better solubility for H<sub>2</sub>S gas in the liquid phase for degradation to occur. The solubility of gases in the liquid is governed by Henry constant. The equation for Henry constant as stated in equation 3.5 is,

$$K_H = C_g/C_i$$

3.5

$K_H$	dimensionless Henry constant	
$C_g$	gas phase concentration	$\text{g m}^{-3}$
$C_i$	liquid phase concentration	$\text{g m}^{-3}$

For pollutant with high Henry constants such as  $\text{O}_2$  and  $\text{H}_2\text{S}$ , the mass transfer is inferior. Thus the better solubility interface with optimal water content is needed. Bio filters usually have less water content (40 - 60 %) as compared to biotrickling filters where the water content is higher thus favoring better degradation.

Table 3-8: Experimental conditions with Removal efficiency for each Empty bed residence time (EBRT)

Experiment	EBRT (s)	[ $\text{H}_2\text{S}$ ] inlet (ppm)	[ $\text{H}_2\text{S}$ ] outlet (ppm)	Removal efficiency (%)
1	250	1,000	< 5	99
2	126	1,000	8.2	99
3	62	1,000	25.2	97
4	43	1,000	42	95

The interfacial resistance mainly exists in the liquid film. This can be controlled using recirculation of liquid contents as in all bio trickling filters in combination with an optimal gas residence time. The rate of recirculation by trickling the liquid along the reactor bed influences the mass transfer process. Usually, the mass transfer occurs from gas to liquid and then to the biofilm. Cox and Deshusses, (2002) described the pollutant elimination activity that occurred in recirculating liquid. Minimum trickling recirculation of 180 ml/min was maintained in the system. This ensured that the packed bed is at least partially wetted. Thus estimating the trickling rate and optimum EBRT is essential and is the critical parameter in designing a bio trickling filter as it directly relates to the pollutant removal. Also, doubling the EBRT requires greater media bed volume. It is to be mentioned that EBRT is based on the packed bed volume and not the void space packing. Similar bio trickling filters EBRT have been reported by Fortuny *et al.* (2011). Dissolution of  $\text{H}_2\text{S}$  into the liquid phase alone does not guarantee that adequate degradation would take place. Thus the evolution of pH variation and sulfate production should also be considered.

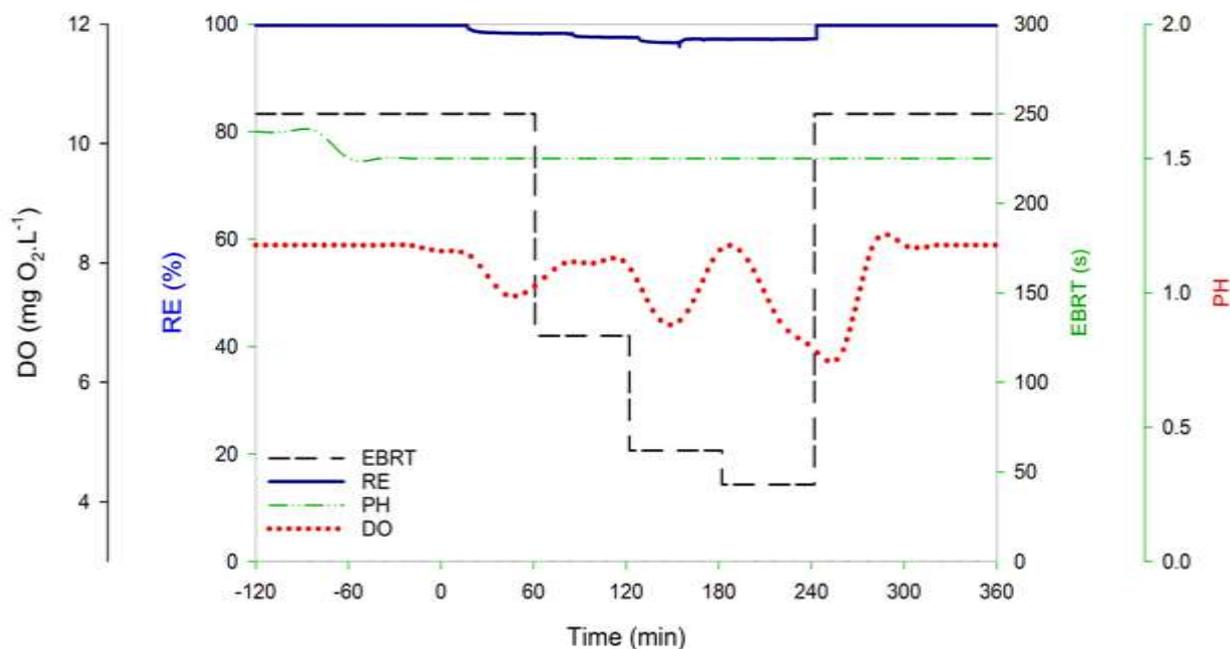


Figure 3.7: Variations in the Removal efficiency (RE), dissolved oxygen (DO) and pH as compared to Empty bed residence time (EBRT). EBRT with 250 s showing maximum removal efficiency of 99 %. pH remained the same (1.5) with negligible fluctuations. Each EBRT was maintained for 1.5 h.

### 3.3.5 Effect of Dissolved Oxygen (DO) and sulfate production

Initial slow pH drop was observed during the experiments which stabilized later as shown in figure 3.7. This may be due to the initial acclimation and slow adaptation of the bacterial culture. Inoculating the reactor with appropriate bacteria reduces the startup period of the reactor significantly (Smet, 1996). However, the system quickly showed stable removal efficiency. The pH was between 1.5 - 1.7 throughout the process. This is due to the presence of Sulphur oxidizing bacteria (SOB) that generate acidic by-products that tend to lower the surrounding pH environment. Though the optimal pH is around 2.0, Yen and Brune, (2007) described that the bacterial activity could be high even at  $\text{pH} < 0.5$ . Alkaline pH is not favored in sulfide oxidization due to the presence of higher residual sulfide and transitional products such as  $\text{S}_2\text{O}_3^{2-}$  and polysulfide which will decline the SOB activity (Krishnakumar *et al.* 2005).

To keep the pH level above 0.5, the fresh nutrient solution was added as a makeup liquid. The nutrient liquid obtained from the recirculation liquid from desulphurization tower served as a source of nitrogen, phosphorous and other trace elements. Sulfide

oxidizing bacteria exists in temperature up to 100 °C (Rawlings, Tributsch and Hansford, 1999). Lems and Dirkse (2009) mentioned the optimal temperature to be 25 - 30 °C which was maintained in this experimental trial. It was observed that there was no significant difference in removal efficiency at either ambient room temperature or above 35 °C. To analyze the requirement of dissolved oxygen (DO) in the process, experimental trials were made with discontinuous oxygen supply after the initial operation, and the entire reaction fluctuation was studied. Discontinuous oxygen supply showed significant variations in H<sub>2</sub>S removal. In general, due to low oxygen solubility, the pollutant degradation in biotrickling filters suffers a mass transfer limitation. Kennes and Veiga, (2002) mentioned that the elimination capacity of the biotrickling filter increased when the partial pressure of oxygen in the gas increased. Mirpuri *et al.* (1997) stated that at high inlet pollutant concentration, removal efficiency in biotrickling filters becomes more sensitive to the oxygen-related parameter. This is because, at high pollutant concentration, oxygen limitation occurs. Figure 3.8 shows at a high loading rate of 85.713 g S m<sup>-3</sup>, the DO concentration in recirculation liquid ranged between 6 - 6.5 mg O<sub>2</sub> L<sup>-1</sup> whereas for loading rate of 14.285 g S m<sup>-3</sup>, the DO concentration maintained well above 8.0 mg O<sub>2</sub> L<sup>-1</sup>.

Control of oxygen in aerobic biotrickling filters has been widely studied as too little oxygen may result in incomplete oxidation of sulfide (elemental sulfur) whereas too high oxygen results in dilution. The occurrence of oxygen limitation depends on the utilization rates of oxygen and pollutant and diffusion into the biofilm respectively. However, the latter can be better enhanced using aeration of the recirculating liquid. The aeration of the recirculated liquid would also facilitate the better supply of dissolved oxygen to the pollutant-degrading microorganisms (Bugu and Labat, 2013). Aeration of recirculated liquid at low pH resulted in high removal efficiency up to 99 % (Montebello *et al.* 2010) and 97.3 % (Charnnok *et al.*, 2013). The ratio of pollutant degradation and oxygen consumption follows the reaction stoichiometry. When the aeration was stopped, sulfate production drastically reduced (results not shown). One of the significant parameters in acid gas treatment is the formation of metabolic products. The major metabolic products in H<sub>2</sub>S treatment as claimed by Chung, Huang, and Tseng, (1996) were elemental sulfur and sulfate. Sulfate is produced under aerobic conditions by sulfur-oxidizing bacteria. Figure 3.8 shows the variations of sulfate production concerning given EBRT and loading rate in each experimental trial. Within few hours of experimental startup, sulfate concentration started to increase in the recirculation liquid. It was found when pH decreased 2 to 1.5; the sulfate concentration increased from 0.06 to 24.7 g/L when analyzed. Thus monitoring of sulfate (S-SO<sub>4</sub><sup>2-</sup>) in the system aids in understanding the microbial metabolism of H<sub>2</sub>S pollutant degradation. The kinetics of H<sub>2</sub>S pollutant elimination follows the first order kinetics, and it depends on various factors including substrate availability. Cox and Deshusses, (2002) mentioned it by

stating in equation 3.6. It should also be taken into account that some bacteria can oxidize elemental sulfur to ( $S-SO_4^{2-}$ ).

$$dc/dt = [(\mu/y_{xs})+m] X \quad 3.6$$

$C_s$	The concentration of substrate dissolved in liquid	$g\ m^{-3}$
$\mu$	growth rate	$g\ g^{-1}\ h^{-1}$
$Y_{xs}$	The yield of dry cell weight per mass of substrate metabolized	$g\ g^{-1}$
$m$	maintenance energy consumption	$g\ substrate^{-1}\ h^{-1}$
$X$	Dry cell weight of biomass in biofilm	$g\ m^{-3}$

These values are, however, difficult to obtain. This is because the growth of sulfide-oxidizing bacteria in the biotrickling reactor is often minimal compared to sludge based reactors. All the energy released during the degradation of pollutant is used for maintenance of biofilm.

Table 3-9: Experimental conditions with variations in sulfate production for each loading rate

Experiment	[H <sub>2</sub> S] LR (g S-H <sub>2</sub> S m <sup>-3</sup> .h <sup>-1</sup> )	[H <sub>2</sub> S] inlet (ppm)	[S-SO <sub>4</sub> <sup>2-</sup> ] produced (g/L)
1	14.285	1,000	0.7
2	28.571	1,000	21.2
3	57.428	1,000	24.0
4	85.713	1,000	34.1

Though sulfate was predominant in the recirculation liquid, at higher loading rates the [(S-SO<sub>4</sub><sup>2-</sup>) / H<sub>2</sub>S] produced ratio was less compared to lower pollutant loading rate. Since the O<sub>2</sub> supplied was constant throughout the process, at higher inlet H<sub>2</sub>S concentration, oxygen limitation occurred resulting in less sulfate production. This proves that greater the oxygen limitation, lesser will be the produced sulfate (S-SO<sub>4</sub><sup>2-</sup>) in the recirculation liquid.

Operating conditions and the environment exert selective characteristics on microorganisms resulting in the development of a specific microbial community. This is proven as the inoculum obtained from desulphurization plant contained a significant amount of elemental sulfur and sulfate in it (Sorokin *et al.* 2016). Though elemental

sulfur was not directly measured during the process, elemental sulfur particles  $S^0$  accumulation was easily noticeable along the reactor bed. Figure 3.8 shows the amount of sulfate ( $S-SO_4^{2-}$ ) produced concerning each EBRT and dissolved oxygen concentration. Each time the EBRT is decreased, the loading rate of the system is increased, and high sulfate production was observed. Similarly, dissolved oxygen consumption was also more for every increased sulfate production.

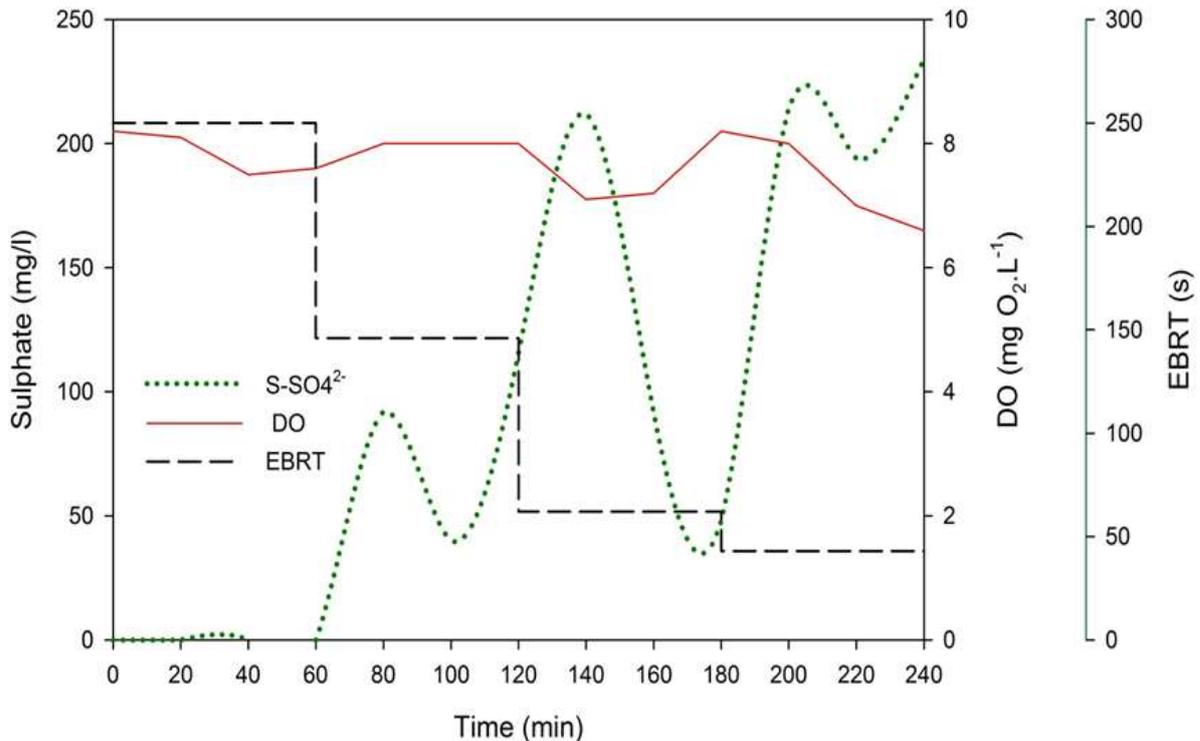


Figure 3.8: Effect of Empty bed residence time (EBRT) on sulfate production. Sulfate production increased in recirculation liquid by decreasing the EBRT. Dissolved oxygen showed significant fluctuations with increasing sulfate production

Meikel Fernandez et al in 2014 observed that 70 % of the by-product in the biotrickling filter was elemental sulfur when working at high loading rate ( $164 \text{ g of H}_2\text{S m}^{-3} \cdot \text{h}^{-1}$ ). Thus sulfate production and accumulation of sulfur shows that the biological oxidation of  $\text{H}_2\text{S}$  has occurred apart from chemically dissolving into water.

It should also be taken into account that some bacteria can oxidize elemental sulfur to  $\text{SO}_4^{2-}$ . Often, biotrickling filters are designed for nonreusable end products. However, De Vegt and Buismann (1996) developed a sequence of biotrickling filters that enable recovery of elemental sulfur as a sulfur powder. Results show that the concentration of

elemental sulfur >7 g/l, can inhibit the elimination of H<sub>2</sub>S (Williams and Kelly, 2013). However, in this system, the renewing of recirculating liquid ensures maximum concentration of 2.3 g/l was maintained.

### 3.3.6 Elimination capacity (EC) vs. loading rate (LR)

The ability to remove gaseous pollutants can be expressed as elimination capacity (EC) and removal efficiency (RE). The calculated EC and RE concerning the given loading rate during the experiments are shown in figure 3.9.

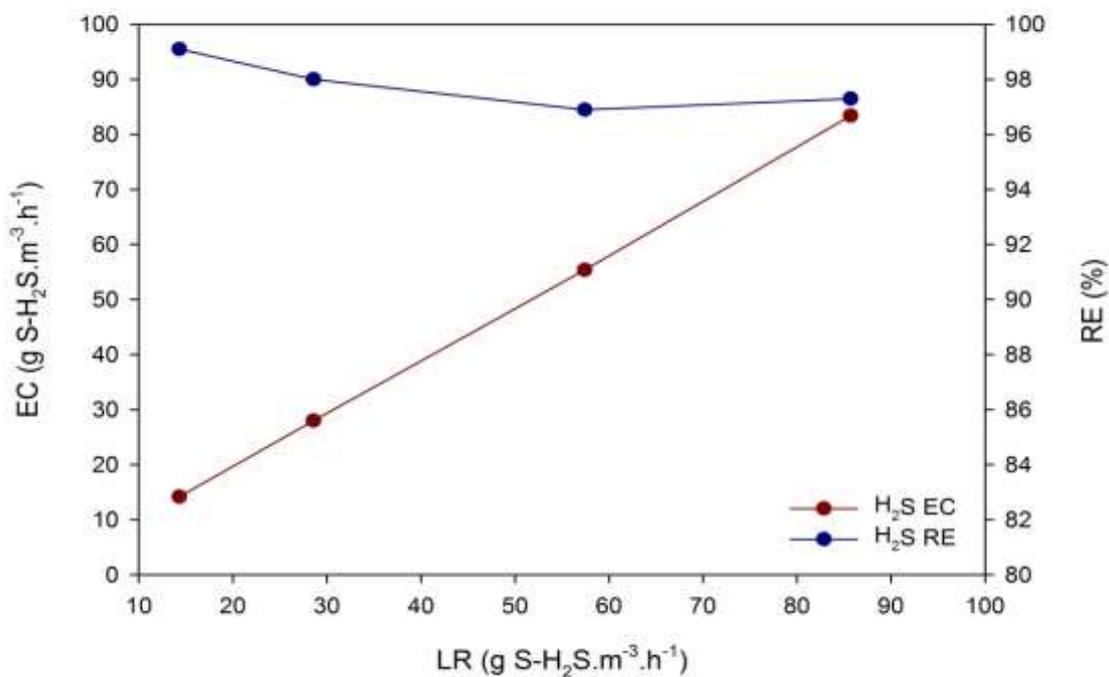


Figure 3.9: Effect of Loading rate (LR) versus Elimination capacity (EC) and Removal efficiency (RE) in the biotrickling filter. Removal efficiency increased with increasing Loading rate. Elimination capacity decreased after reaching the critical loading rate.

The elimination capacity increased when the loading rate was increased. The maximum elimination capacity was found to be 85.7 g S - H<sub>2</sub>S m<sup>-3</sup>.h<sup>-1</sup>. Results show that the removal efficiency dropped at the same inlet concentration but with a shorter retention time (EBRT). This decrease in removal efficiency may be due to mass transfer

limitation. As mentioned in the study (Charnnok *et al.*, 2013), elimination capacity depends on the mass transfer of dissolved gas pollutant into biofilm combined with microbial degradation. When the mass loading rate is below a critical value, the elimination capacity is equal to the given loading rate and the removal efficiency is close to 100 %. This follows the first order kinetics and is expressed in Michaelis-Menten equation described in equation 3.7. After reaching the critical elimination capacity, the removal efficiency no longer increases. Thus the elimination capacity follows zero order kinetics, and it is no longer dependent on mass loading rate. This parameter is mainly used for designing a bio trickling filter.

$$EC = EC_{\max} * L_s / L_s + A \quad 3.7$$

$L_s$	inlet H <sub>2</sub> S inlet loading rate	$g\ m^{-3}\ h^{-1}$
$EC_{\max}$	maximum elimination capacity in the biotrickling filter	
A	half the saturation constant or H <sub>2</sub> S loading rate at 0.5 $EC_{\max}$ .	

According to the results obtained; the critical elimination capacity was obtained at 62 s beyond which there was no significant rise in elimination capacity. At this stage, the sulfate formation was also higher as 0 - 75 % indicating a complete oxidation level. Results also show that high performance was still seen in the biofilter though the removal efficiency (RE) values dropped. This shows that the system can perform the H<sub>2</sub>S removal. The critical EBRT is found to be 62 s which is considered normal in biotrickling filtration of H<sub>2</sub>S (Sercu *et al.* 2005).

Further decrease in EBRT to 43 s showed a decrease in removal efficiency. It also affected dissolved oxygen (DO) as it dropped down from 8 mg/L to 6 mg/L. Thus it is inferred that the central limiting process was due to mass transfer limitation of O<sub>2</sub> and low solubility of H<sub>2</sub>S at reduced gas contact time (Fortuny *et al.* 2011). At this point, the biofilm suffers an oxygen limitation, and hence the microbial community has starvation for O<sub>2</sub>. Thus Jin, Veiga, and Kennes,( 2007) indicated that the decline in removal efficiency as a result of incomplete degradation is due to diffusion limitation and reaction limitation.

While the former is explained above, latter could be due to the microorganisms themselves not involved in the degradation process. Higher mass loading rate could result in toxicity of microorganisms and inhibition of sulfide-oxidizing bacteria. Other

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factors may also include, shortage of nutrients, substrate availability, etc. Once the experimental period was finished, the reference operation was resumed, and RE was soon to show 99 %. This shows a quick recovery capacity of the system studied

### 3.3.7 Microbiological FISH analysis

Removal of H<sub>2</sub>S using *Thiobacillus* spp in acidic biofiltration has been extensively studied in the various literatures (Zhang *et al.*, 2009), (Han, Zhang, and Xu, 2011), (Charnnok *et al.* 2013). The extremely low pH of the inoculum (1.5 - 3.2) and the high concentration of elemental sulfur and sulfate ascertain the presence of *Acidothiobacillus* spp genus. Fluorescently labeled probes THIO1 and ALF 968 targeting the *Acidothiobacillus* spp genus and the related alphaproteobacterial species is shown in figure 3.10. The underlying physiology of sulfide, sulfur and thiosulfate oxidation in *Acidothiobacillus* spp is evident as the environment containing this particular species is hugely acidic, toxic, sulfur-rich and iron-poor (Macalady, Jones, and Lyon, 2007). Some bacterial species that are closely related to *Acidothiobacillus* spp genus (Gammaproteobacteria) are the members of genus *Acidiphilium* (Alphaproteobacteria) which is evident as well in this case (Lenk, 2011). A significant number of cells were also highlighted when the probe EUB338. It is to be noted that genus *Acidiphilium* (Alphaproteobacteria) are often associated with Gammaproteobacteria in iron and sulfur-oxidizing environments. (Harrison, 1983). Dumont (2015) suggest the presence of other H<sub>2</sub>S degrading microorganisms has an enhanced effect and the ability to remove H<sub>2</sub>S. Studies show that *Acidiphilium* spp. remove toxic organic compounds for *Acidothiobacillus* spp genus (Johnson and Hallberg, 2005); (González-Toril *et al.* 2003). The ALF probe 968 was used to detect this group of bacteria which showed positive results. It is believed that Autotrophic sulfur oxidizers use the energy gained from sulfur oxidation to assimilate carbon dioxide into organic biomass. To study the ability of CO<sub>2</sub> fixation, the bio trickling filter operation was initially carried out by the addition of carbonate as an inorganic carbon source. During combined removal process operation (see chapter 5), the carbonate supply in the biotrickling filter was stopped. It was enriched with gaseous CO<sub>2</sub> supply from the biogas mixture. The FISH analysis was again performed at regular intervals of 53, 95, 124 days. During the entire process, FISH results were essentially the same, hence confirming the stable microbial population. This shows the ability of sulfur-oxidizing bacteria to thrive under different CO<sub>2</sub> supplementation.

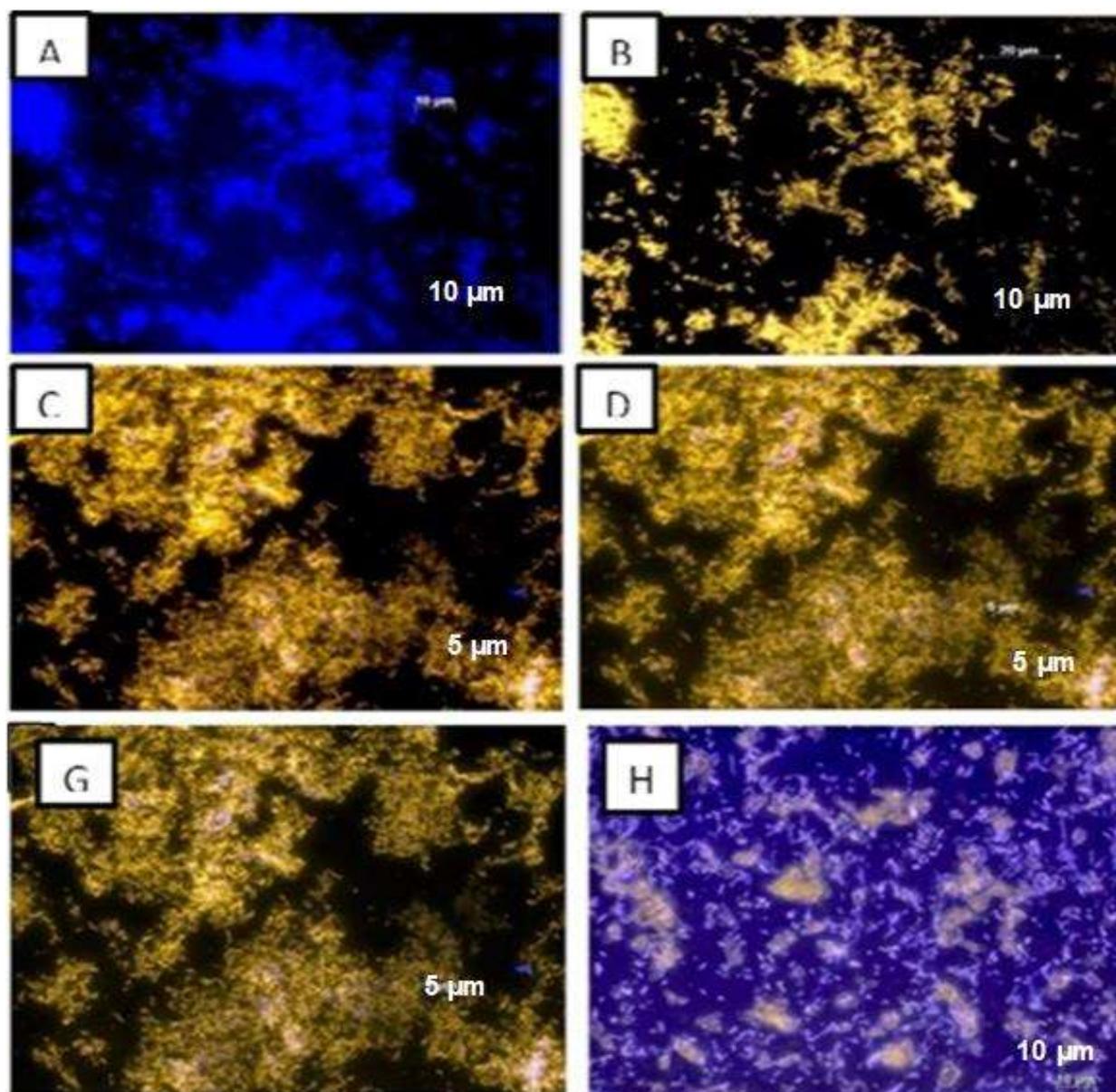


Figure 3.10: Fluorescence pictures of bacteria from the biotrickling filter. A) and B) DAPI stained cells and THIO 1 labeled cells from the inoculum sample before acclimatizing in the biotrickling filter, Bar 10 µm; C) D) and G) samples from the biotrickling filter after acclimatization with H<sub>2</sub>S. Samples were hybridized cells with THIO probe, bar 5 µm; H) hybridized cells with ALF 98 probe specific for *Acidiphilium* spp, Bar 10 µm.

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## 4 Carbon dioxide capture from biogas using carbonation of bottom ash

### 4.1 Material and method

This research aimed to assess the interaction of bottom ash with the CO<sub>2</sub> present in biogas. Municipal solid waste bottom ash is a highly reactive material towards atmospheric CO<sub>2</sub>. By speeding up the natural weathering process called carbonation, it was possible to determine the maximum CO<sub>2</sub> uptake efficiency. Carbonation of bottom ash was studied in detail to optimize the given process for biogas upgrading. The primary variables tested were particle size and moisture content and sorption capacity. The finest fraction of bottom ash showed the best performance with a liquid/solid ratio of 0.1. The sorption capacity was found to be 14.56 g CO<sub>2</sub>.kg<sup>-1</sup> with hydrated bottom ash.

Incineration is currently the most widespread technology in for treating of municipal solid waste (MSW). This process not only produces heat or energy required but also reduces the enormous amount of volume by reducing the waste mass to 70 % and volume by 90 % (Zermeño *et al.* 2015).

Non-biodegradable waste in MSW usually produces two types of incineration residues such as Bottom ash (BA) and air pollution control (APC). The study of interest in this project is mainly bottom ash which is frequently reused after stabilizing with weathering. Weathering is the absorption of CO<sub>2</sub> from the atmosphere that chemically converts CaO and other oxides present in bottom ash to CaCO<sub>3</sub>.

The study revealed that after the carbonation process, there was an increase in bottom ash weight. The final product was characterized by a reduction of pH in bottom ash sample. Biogas typically has the CO<sub>2</sub> content of 30 - 50 % depending on the substrate in anaerobic digestion, a product which is a good source for carbonation of bottom ash. Thus, this process could be exploited further in biogas upgrading as its interesting mainly for its use in municipal solid waste (MSW) management.

#### 4.1.1 Design of carbonation reactor

The experimental trials for CO<sub>2</sub> removal using absorption was carried out using separate reactor designed for the purpose. The experiments were conducted at lab scale at the University of Duisburg-Essen. The reaction chamber was a cylindrical column made up of plexiglass. The diameter of the reactor was 150 mm, and its height was 62 mm. To lower pressure drop and avoid wall effects, larger bed diameter was used. This is achieved when the ratio between mean particle size diameter of the absorbent to the inner diameter of absorption column is greater than 10 (Miao, 2011).

The reactor was utilized as an adsorbent bed. The reactor was equipped with an opening on the top for loading and unloading of the adsorbent (bottom ash).

For experimental purpose, different size fraction of bottom ash (size 0 - 2 mm, 4 mm, 8 mm) obtained through sieving was initially packed into the reactor. The reactor consisted of a perforated plate at the bottom to ensure a free gas flow. The term “carbonation reactor” introduced by Mostbauer *et al.* (2014) was used in this study.

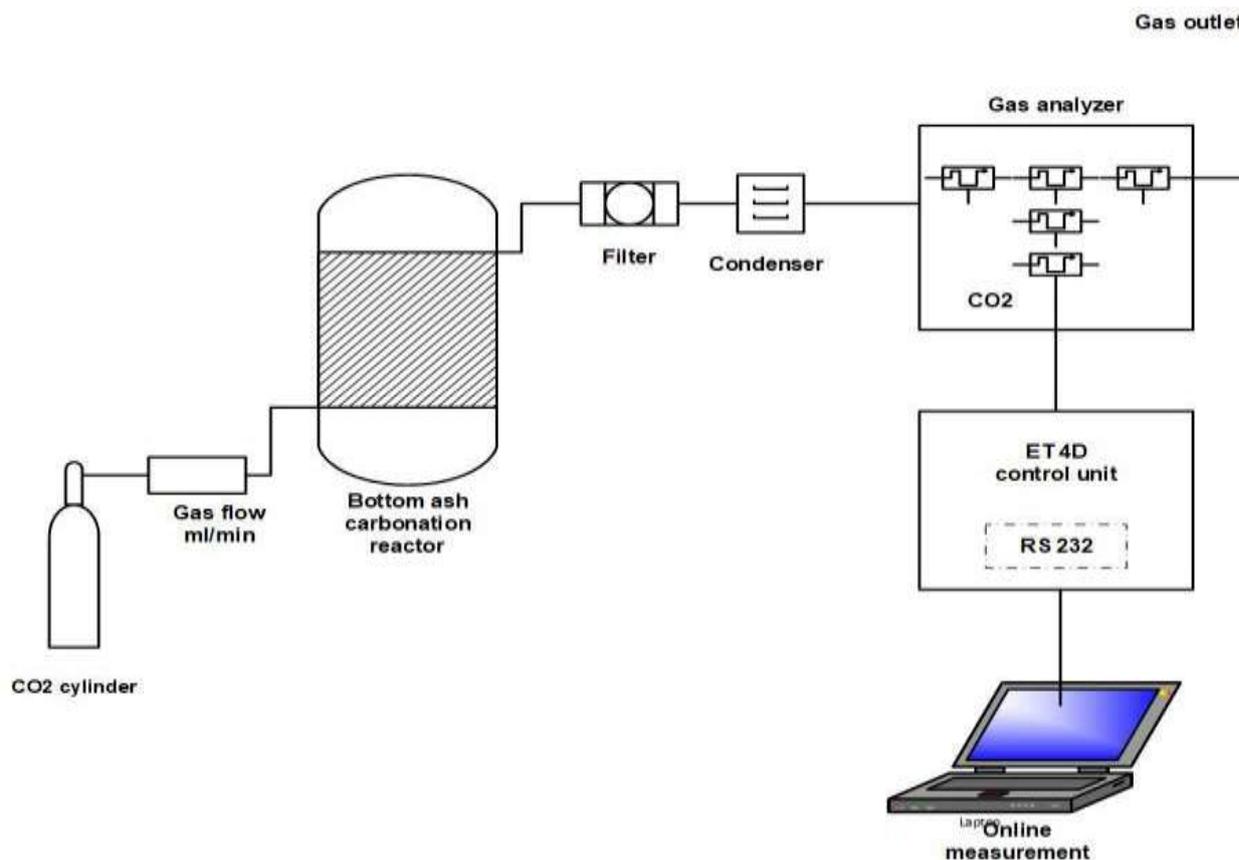


Figure 4.1: Process layout for the experimental design on bottom ash CO<sub>2</sub> removal. The gas from gas cylinder passes through the bottom ash reactor where CO<sub>2</sub> is absorbed. The exit gas is using the gas analyzer.

Bottom ash also rested on the perforated plate which retained the bottom ash particles and allowed free gas flow. The reactor at the bottom contained ample space for gas accumulation in the chamber before reaching the reactant bed. Synthetic gas stream (99.8 vol % CO<sub>2</sub>) at standard temperature and pressure was supplied by compressed gas cylinder obtained from Linde company (Germany) was passed into the reactor accompanied by N<sub>2</sub> flushing at regular intervals.

The gas mixture was passed through the reactor bed from the bottom to the top (countercurrent mode) and exited at the top connected to the gas analyzer.

Different carbonation tests were performed according to the Table 4-2. The duration of each experiment is determined according to the breakthrough time of CO<sub>2</sub>. The breakthrough time is considered as the saturation point for bottom ash when CO<sub>2</sub> concentration at the outlet is same as that of the inlet.

#### 4.1.2 Experimental conditions

Prepared bottom ash samples contained in quartered splits were used for this study. Each sample was sieved with different size fractions ranging from 0 - 2, 0 - 4, and 8 mm and filled into the reactor bed of the bottom ash reactor as shown in figure 4.1. Table 4-2 shows various experimental trials with different size fractions. Finest fractions show better absorption capacity according to del Valle-Zermeño *et al.*(2015). Hence the reactor was packed with 400 g of 0 - 2 mm samples initially. To study the effect of moisture content different liquid/solid ratio (L/S) was taken into consideration. Nitrogen gas was used to purge the reactor before the start of the experiment. Pure CO<sub>2</sub> gas was fed into the reactor at a minimal flow rate of 10 ml·min<sup>-1</sup>.

The output gas regarding volume percent (Vol %) was continuously analyzed using the ET-4D gas analyzer for measuring CO<sub>2</sub>. The first reading was taken after 5 min after starting the gas input, and subsequently, sampling was done at 15 min interval. When the gas composition at the outlet was detected to be similar to gas inlet, the experiment was stopped.

This is considered as the breakthrough time of bottom ash. The wet bottom ash is then removed and tested for weight and pH.

#### 4.1.3 Bottom ash collection

Fresh bottom ash, quenched and obtained from the municipal solid waste incinerator from the company MSWI AVEA Entsorgungsbetriebe GmbH & Co. KG, located in Leverkusen, (Germany) was used for the entire project. AVEA (Aufbereitungs- und Deponierungsgesellschaft) GmbH operates the Waste Disposal Centre Leppe in Lindlar-Remshagen in the Oberbergisch region. It is owned by the BAV (Bergisch Waste Management Association) which operated the landfill site in Leppe since 1982. The facility consists of domestic waste industrial waste treatment using thermal incineration process. Since its commissioning from 1970, the plant has obtained a thermal throughput of 210,000 tonnes with thermal treatment of waste from 800,000 inhabitants. The plant is also equipped with energy recovery system whereby the electricity demand of 20,000 households in Leverkusen is covered.

Table 4-1 shows the operational data of the plant published in ISWA (International solid waste association) 6th edition report in August 2012. (ISWA, 2012)

Table 4-1: Technical details on bottom ash production from AVEA Leverkusen Incineration plant

Location	Bottom ash (tonnes)	Fly ash (tonnes)	Steam produced (tonnes)	Electricity produced (MWh)	Electricity sold (MWh)	Heat sold(MWh)
Leverkusen	56000	2300	620,000	44	9.5	150

Operational data 2004, source AVEA GmbH, Germany

The thermal treatment of waste is carried out in combustion boilers at a temperature around 1,100-degree Celsius. After complete combustion, bottom ash is collected at the bottom of the furnace and quenched immediately. Collected bottom ash further underwent treatment such as primary and secondary shredding, sieving, size separation, magnetic separation and other processes such as glass particles removal before stored for further analysis. Usually, bottom ash particles less than 2 mm is called fine fraction, and less than 45 mm is called coarse fraction.

Samples of bottom ash used for the study was collected directly from the pile of bottom ash stored in weathering area. Fresh Bottom ash reacts with water and releases  $H_2$  and heat thereby undergoing hydration and oxidation (Mostbauer *et al.* 2012)

Bottom ash could absorb  $CO_2$  present in the atmosphere when hydrated thus undergoing carbonation reaction. It can be presumed that few some amount of bottom ash would have undergone carbonation. To avoid further contact with water, bottom ash was sealed in airtight containers and stored until further required. Stored bottom ash samples were analyzed for initial moisture content (12.6 wt %), and pH before the start of each experiment.

Figure 4.2 shows the location of bottom ash collection used for experimental purpose



Figure 4.2: Images of bottom ash collection from AVEA GmbH, Leverkusen, Germany (Rajavelu 2016).

The experiments were performed on samples of bottom ash both freshly produced, as well as from the stored containers. For each experiment, 500 kg sample, was initially dried at 80 - 100°C in an oven. Drying duration has been obtained through preliminary tests. Ash particles were then sieved again and mixed for homogenous distribution of particles. During mixing water is sprayed to obtain different L/S ratio from 0.05 to 0.4. The samples were then quartered to obtain the representative splits required for experimental trials.



Figure 4.3: Images from AVEA GmbH, Germany. Pictures are showing municipal waste handling as well as incineration inside the furnace (Rajavelu 2016).

## 4.2 Analytical Methods

### 4.2.1 Gas Analysis

The gas used for the experiment was technical grade  $\text{CO}_2$  >99.8 % obtained from compressed gas cylinder purchased from company Linde GmbH (Germany). Input and out gas flow rates are varied throughout the experiment and controlled by variable PTFE flow from meters Cole Parmer company (Germany) with metering range 0.5 ml/min - 500 ml/min. Continuous online gas analyzer from ExTox company (Germany) was used to measure the input and output volumetric  $\text{CO}_2$  gas composition using infrared absorption (accuracy +/- 3 %). The pressure developed along the packed bed column was measured using pressure transducer model PX119 – 100GI Omega company (Germany). Pressure and temperature of the system were monitored discontinuously whereas the gas flow was measured continuous by online gas analyzer system. The measured data was transferred to PC using programmable ExTox Data Logger ET-SL. Nitrogen was required to flush the system connected to sensors as well

as to explicit unwanted air locks in bottom ash particles. Thus the gas flow meter is also connected to nitrogen system in the laboratory in order to facilitate nitrogen bypass into the flow meter during the experiments.

#### 4.2.2 Solid Analysis

The weight of bottom ash (kg) was tested before and after each experiment. The initial moisture content of the sample was (12.6 wt %). Different samples ranging from 5 to 20 wt % were prepared for experiments. The water content of the sample was tested by measuring the weight of the sample initially and oven drying at 60°C and measuring again. The difference in sample weight gain was denoted as the moisture content present in bottom ash

The pH of bottom ash was also investigated before and after carbonation. The following procedure was adopted for measuring pH of the sample before and after CO<sub>2</sub> absorption.

1. 5 g of the untreated and treated bottom ash was mixed with 50 ml Millipore water so that the liquid-to-solid ratio (L/S) = 10 L kg<sup>-1</sup> is maintained.
2. The beaker containing the liquid sample is continuously stirred using magnetic stirrer at high rpm for 24h. This is the average time leaching can occur in a given bottom ash sample.
3. Later, the sample is filtered through 45 um, and the pH was measured.

#### 4.2.3 Sorption capacity measurement

During the experiment, CO<sub>2</sub> is dissolved in water forming bicarbonates, which later reacts with oxides of bottom ash. When dissolved CO<sub>2</sub> reacts with calcium oxide in bottom ash, calcite (CaCO<sub>3</sub>) is formed that induces an increase in sample mass which is related to the amount of CO<sub>2</sub> trapped in bottom ash.

$$V_{CO_2} = \left(\frac{RT}{P}\right) \times \frac{\Delta m}{M_{CO_2}} / (100 - h)m_i \quad 4.1$$

$V_{CO_2}$	The volume of absorbed CO <sub>2</sub>	m <sup>3</sup> .kg <sup>-1</sup>
$RT/P$	Gas constant	
$M_{CO_2}$	CO <sub>2</sub> molar weight	Kg.mol <sup>-1</sup>
$m_i$	The initial mass of the sample	Kg
$h$	Moisture content	%

This can be determined experimentally by the difference in initial and final mass of bottom ash. The mass balance analysis will give an idea of the carbonation reaction occurred during the experimental trial. The difference in the mass as a result of CO<sub>2</sub> sorption in bottom ash was calculated by Rendek, Ducom, and Germain, (2006) as given in equation 4.1. Sorption capacity measurements were carried out with varying liquid to solid ratios (L/S) as shown in figure 4.5

### 4.3 Results and Discussion

Each experiment consisted of reactor filled with fresh Bottom ash (wet) tamped in bed and flushed with N<sub>2</sub> gas before carbonation reaction was started. Test no 4, 5, 6 showed no breakthrough time. It can be that at such a high flow rate (500 ml/min) there was not enough gas contact time. Also, the concentration of CO<sub>2</sub> is high (vol % 99.8). As shown in figure 4.4, the breakthrough time for test 1 occurred after 40 min.

Table 4-2 Experimental trials for bottom ash carbonation by gaseous CO<sub>2</sub>

Test no	1	2	3	4	5	6	7
Grain size	0 – 1 mm	0 – 1 mm	0 – 1 mm	0 – 2 mm	0 – 2mm	0 – 2 mm	0 – 1 mm
Liquid/Solid ratio	0.05	0.1	0.2	0.4	0.2	0.2	0.2
Bottom ash (g)	400	400	400	300	300	200	10
Flow rate (ml/min)	10	10	10	500	90	500	60
Gas composition (v %)	99.8	99.8	99.8	99.8	99.8	99.8	99.8
Breakthrough time (min)	60	60	40	a)	10	a)	a)
CO <sub>2</sub> uptake (g/kg of Bottom ash)	10.96	14.56	12.63	-	-	-	-
pH	9.2 b)	9.1 b)	9.24 b)	-	-	-	-

a) No breakthrough time was observed.

b) Initial pH of noncarbonated bottom ash showed 11.23 (It was performed with Leachate 10 L/kg) with an rpm for 24hr.

Breakthrough capacity was observed when the flow rate was reduced to as low as (10 ml/min), and the bottom ash load (g) was increased. The pattern of the curve followed adsorption isotherm and kinetics as described by Nethaji, Sivasamy, and Mandal, (2013). This shows that enough gas contact time is needed for better carbonation. There was slight heat in the reactor when the reaction was performed. It is proven that literature specifies carbonation is an exothermic reaction.

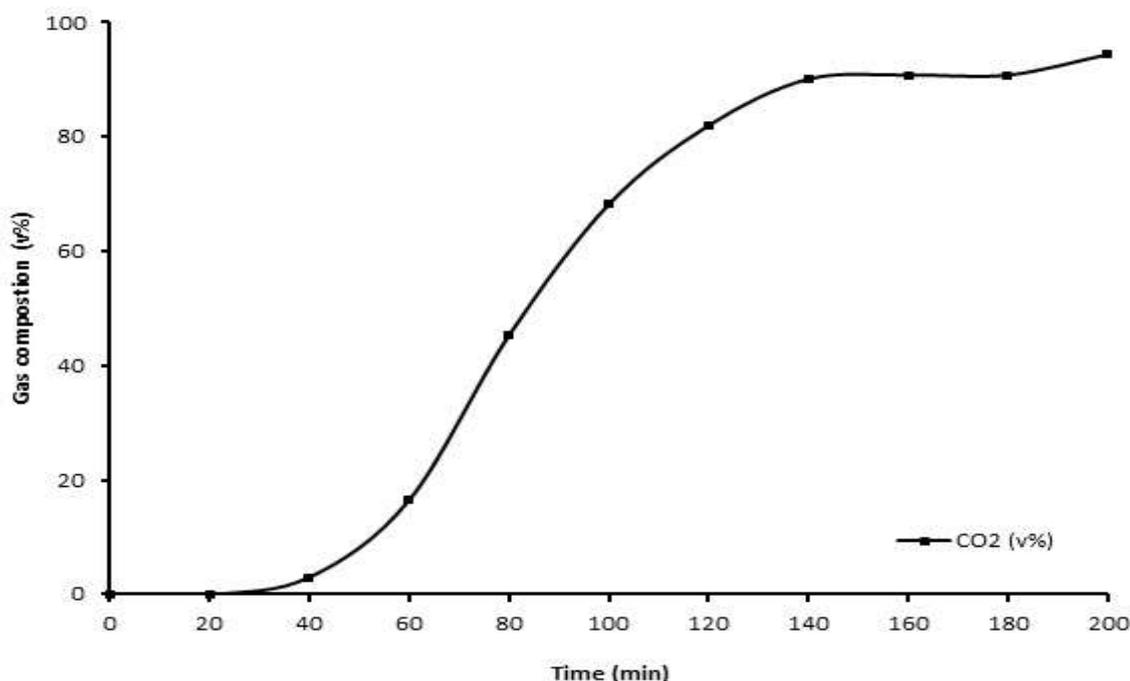


Figure 4.4: Graph showing S-shaped curved obtained with CO<sub>2</sub> gas composition (vol %) versus breakthrough time. The breakthrough time was observed at less than 40 mins after passing the gas.

#### 4.3.1 Effect of moisture content

The study aimed at understanding CO<sub>2</sub> uptake of bottom ash to be integrated into a combined removal process setup. Finding the optimum moisture content of the given bottom ash samples is a prerequisite for a valid carbonation reaction to take place. The moisture in the samples plays a significant role in carbonation. Lin *et al.*, (2015) suggested that optimal moisture resulted in better carbonation of bottom ash. Different liquid /solid ratio (L/S) of the bottom ash samples with size fractions (0-2 mm) was tested for breakthrough time. Results indicate that L/S = 0.1 showed a better breakthrough time of 42 mins (results not shown). It was interesting to note that bottom ash samples with a high L/S ratio led to an earlier breakthrough time. It can be inferred that the earlier breakthrough time of ash samples could be due to incomplete carbonation and hence a quick replacement of bottom ash was required.

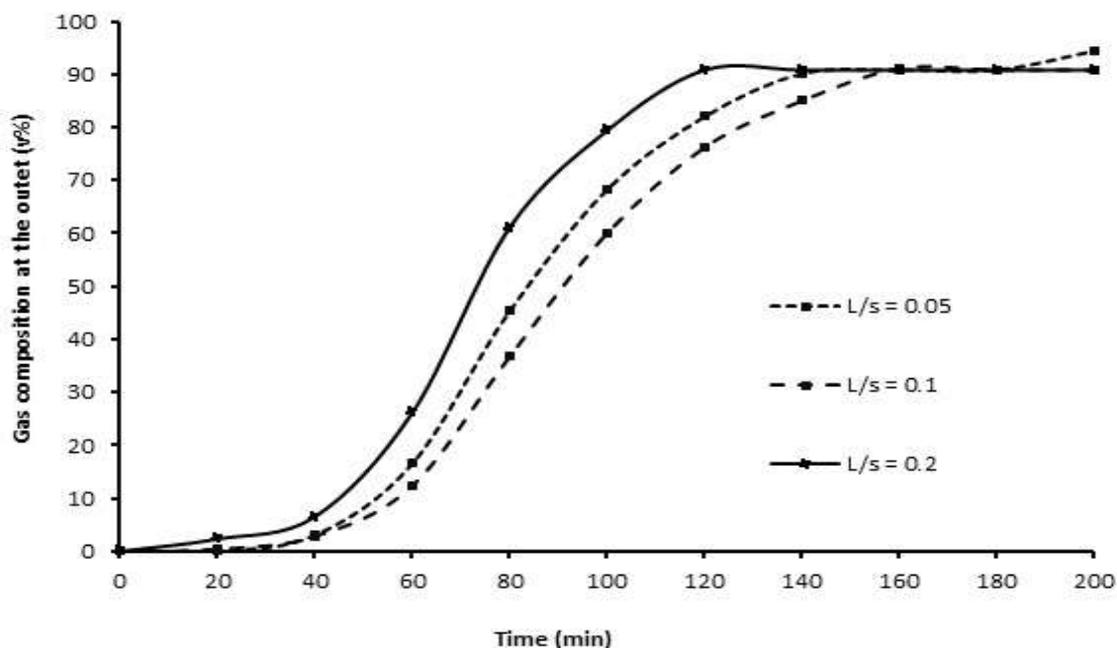


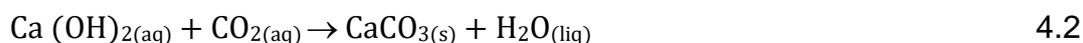
Figure 4.5: Graph with breakthrough curve obtained for different Liquid/solid (L/S) ratio (0.05, 0.1, 0.2) for bottom ash samples. Samples with an optimum moisture content of 0.1 took a long time to attain breakthrough point whereas samples with higher moisture content (0.2) obtained quicker breakthrough time.

During carbonation, the reaction stabilizes bottom ash by changing its mineralogical characteristics. One such parameter is pH. Carbonation modifies hydroxides in bottom ash at a pH 11.5 to carbonates in bottom ash at pH 8.5 - 9 ( Gerven *et al.* 2005). The effect of carbonation on pH is essential regarding its relation to heavy metal leaching. Hence, the pH was measured by diluting the samples with L/S = 10 L/kg (Seniūnaitė and Vasarevičius, 2017); (Kartinen, 2004 ); (Lapa *et al.* 2002). The pH was determined each time before and after the carbonation. Results indicated that the initial pH of 11.23 was reduced to 9.2 after carbonation (Vehlow, 2002). When carbonation occurs, OH<sup>-</sup> ions are consumed, and as a result, the alkalinity is consumed. This causes pH to reduce and mineral such as calcite to precipitate until the material is in equilibrium with CO<sub>2</sub>. However, this reaction is reversible if the precipitate comes in contact with acids (pH 5-7) for example acid rain. The influence of MSWI bottom ash on heavy metal leaching has been subject to study in the various literature (De Boom, Aubert, and Degrez, 2014), (Chimenos *et al.*, 2005) (Arickx *et al.*, 2010) (Van Gerven *et al.*, 2005). The overall effect of carbonation thus may result in changes in mineral properties,

precipitation of metal carbonates combined with pH reduction (Planchon and Nada, 2015). Bottom ash absorption of CO<sub>2</sub> is an exothermic process. Thus heat is released during the reaction which causes some evaporation to occur. Bottom ash weight was measured initially and after carbonation experiment. The wet sample was measured before feeding into the reactor and was measured again after drying and after carbonation. Mass balances obtained through CO<sub>2</sub> fixation and gas analysis showed an increase in weight (g) as shown in table 4-3. It can be concluded that albeit evaporation of water, the sample weight gain measured experimentally ascertains carbonation took place. The above experiments were performed with 99.8 % CO<sub>2</sub>. Decidedly fewer journals report this CO<sub>2</sub> concentration with bottom ash as to many report a lesser CO<sub>2</sub> concentration, (10 %, 50 %, 40 %, biogases mimic). This shows that the concentration does not majorly affect the carbonation process.

### 4.3.2 Upgrading capacity

The ability to uptake CO<sub>2</sub> by the cations present in the bottom ash is quantified regarding upgrading capacity or sorption capacity of Bottom Ash. It is expressed as g of CO<sub>2</sub> sorted per kg of wet Bottom ash as a function of time. During carbonation, gaseous CO<sub>2</sub> reacts with metal oxide bearing materials in the presence of moisture. The main reaction of Portlandite (Ca(OH)<sub>2</sub>) in bottom ash in the aqueous medium is stated by Rendek, Ducom, and Germain, (2006) is given in equation 4.2



Though various other oxides such as amphoteric oxides and acidic oxides can undergo carbonation reaction, basic oxides such as CaO and MgO are the most favorable reacting with CO<sub>2</sub> (Cappai *et al.* 2012). The affinity for CO<sub>2</sub> fixation also depends on factors such as chemisorption strength of CO<sub>2</sub> gas (gas-solid interface), solubility constant K<sub>sp</sub> (gas-liquid interface) and total content in the solid particle.

Thus, the capacity of CO<sub>2</sub> fixation is directly proportional to the amount of binary oxide (CaO and MgO) and hydroxides (Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>) content present in the matrix (Snellings, Mertens and Elsen, 2012). The CaO offers more potential for chemisorption of CO<sub>2</sub> than MgO.

The carbonate precipitates are thermodynamically stable and can fix CO<sub>2</sub> permanently under ambient conditions since they have low energy states than their reactants such as CO<sub>2</sub>. A study on Gibbs free energy indicated that carbonation of calcium ions proceeds at a temperature around 45°C whereas for Magnesium ions the temperature is over 144°C (Guo, Chang and Xie, 2006). This adds to the evidence of calcium oxide carbonation in the given experimental trial.



Figure 4.6: Bottom ash samples before and after carbonation (Rajavelu 2016).

Table 4-3: Mass balance and CO<sub>2</sub> uptake for experimental test trails 1, 2 and 3

Test no	1	2	3
Initial bottom ash mass (g of WS)	423.60	436.84	476.02
Final bottom ash mass (g of WS)	428.12	442.07	479.95
CO <sub>2</sub> fixation using mass balance (g/400g of BA)	4.52	5.23	3.93
CO <sub>2</sub> fixation using gas analysis and flow (g/400g of BA)	5.05	5.825	4.386
CO <sub>2</sub> uptake (g/kg of BA)	10.96	14.56	12.63

\*WS = wet substance; BA = Bottom ash

The exothermic reaction as shown in equation 4.2, forming carbonates is often kinetically limited depending on the type of alkaline oxide that takes part in the reaction. Thus to understand the reaction kinetics, the rate of involved reactions must be understood. The carbonation mechanism of Ca and Mg-bearing oxides occur both via gas-solid and aqueous reactions. The above experimental process occurred through aqueous carbonation explains that the rate of the reaction is dependent on CO<sub>2</sub> hydration and carbonate formation.

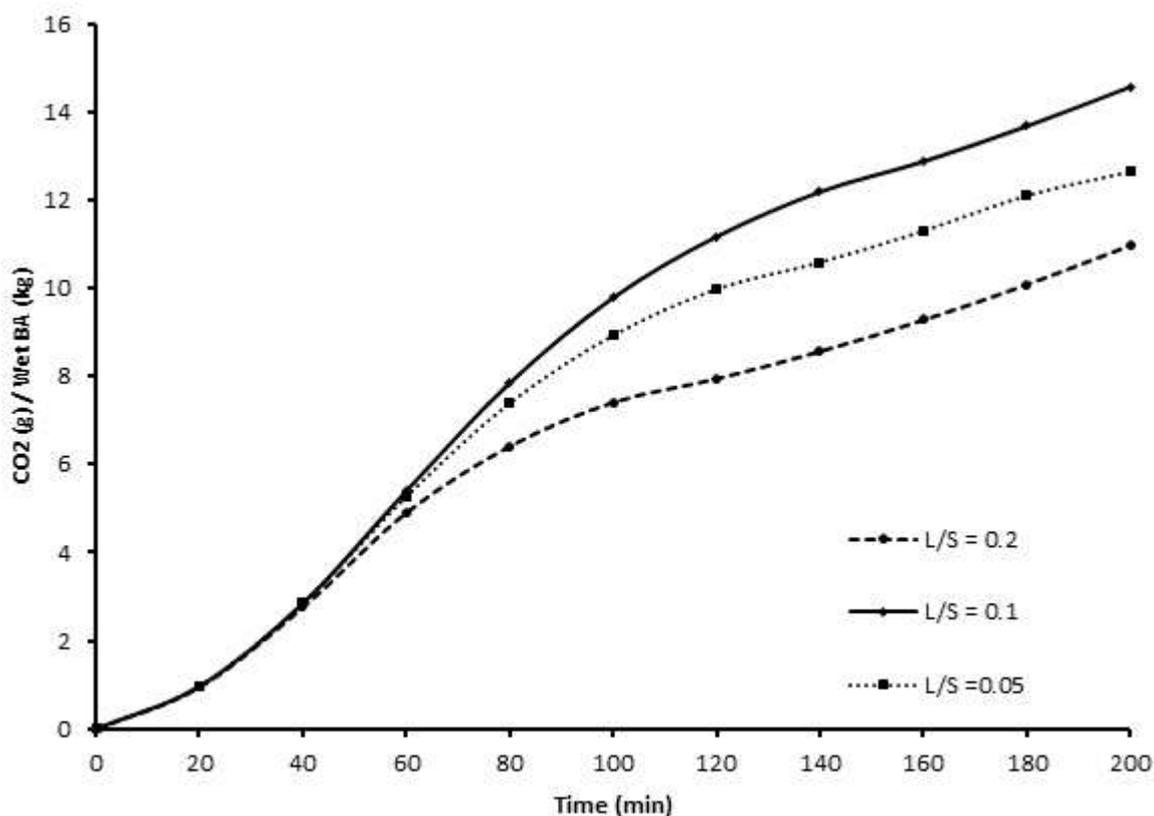


Figure 4.7: Graph of sorption capacity ( $\text{CO}_2$  g/Wet BA (kg)) versus Time (mins). Bottom as samples with Liquid/Solid (L/S) ratio 0.1 showed higher sorption capacity. All samples tested had a size fraction of 0 – 2mm.

Figure 4.6 shows the bottom ash sample before and after carbonation. To further understand the carbonation mechanism and identify the  $\text{CO}_2$  uptake ratio of bottom ash, its sorption capacity was determined through various Liquid/Solid ratios. Figure 4.7 shows the different sorption capacity of the samples tested with different ratios of hydrated samples. It is evident that bottom ash sample containing L/S ratio = 0.1 showed high sorption capacity of  $14.56 \text{ g CO}_2 \cdot \text{kg}^{-1}$  as shown in figure 4. These values are in agreement with those reported by (Mostbauer, Lenz and Lechner, 2008). It is also observed that bottom ash could show high absorption when specific parameters are modified such as an increase in pressure or change of reaction chamber. Lombardi, Carnevale, and Pecorini, (2016) observed that the use of rotating reactor chamber increased the bottom ash  $\text{CO}_2$  uptake greater than  $37 \text{ g/kg}$  of BA. It is clear that higher  $\text{CO}_2$  sorption capacity of the finest fraction is related to the predominance of CaO and optimal moisture content as reported by ( Zermeno *et al.* 2015).

## 5 Lab-scale and pilot test study for combined H<sub>2</sub>S and CO<sub>2</sub> removal process for biogas upgrading

The proposed process for combined H<sub>2</sub>S and CO<sub>2</sub> removal process was investigated as a preliminary analysis at the departmental laboratory of urban water and waste management at University Duisburg-Essen. The laboratory testing was performed to check the operating conditions, safety, process layout and its feasibility of design to be installed later at the biogas production site.

### 5.1 Lab scale material and methods

The experimental scheme for combined H<sub>2</sub>S and CO<sub>2</sub> removal process is shown in Figure 5.1. Two reactors (biotrickling filter for H<sub>2</sub>S removal and carbonation reactor for CO<sub>2</sub> removal) were serially connected using individual pneumatic nozzles.

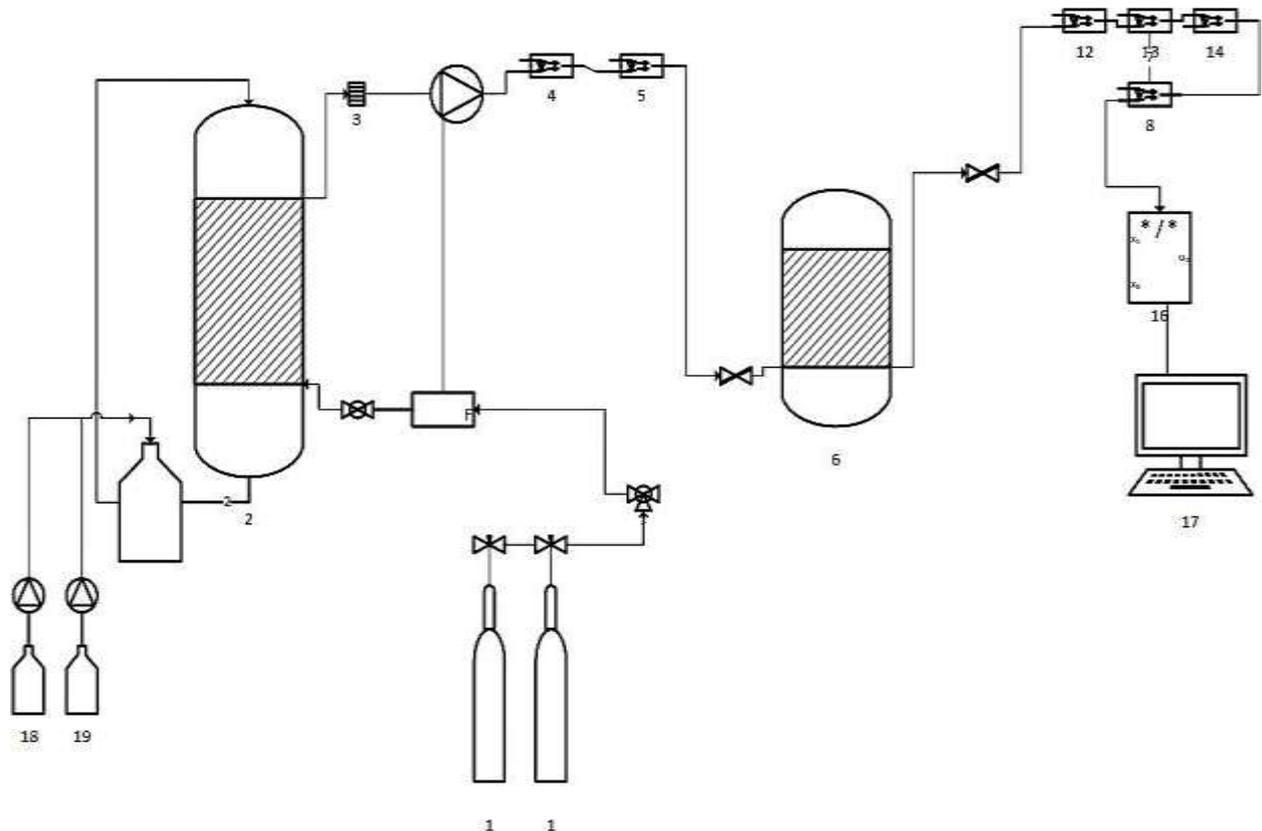


Figure 5.1: Experimental Layout for Combined H<sub>2</sub>S and CO<sub>2</sub> removal process at Labscale. The process and the numbering of equipment are described in section 5.1

The gas mixture [1,000ppm<sub>v</sub> H<sub>2</sub>S; 99.8 vol % CO<sub>2</sub>] was obtained from compressed gas cylinders (1) and was regulated by mass flow controllers (Bronkhorst GmbH, Germany) and mixed using pneumatic mixing valves (Festo GmbH, Germany).

The gas mixture at standard temperature and pressure was introduced first into the biotrickling filter (2) to undergo H<sub>2</sub>S desulphurization. It is then passed through condensate trap (3) to remove excess moisture. The gas exiting the condensate trap passes through gas sensors H<sub>2</sub>S (4) and CO<sub>2</sub> (5) to analyze the concentration. It is then passed through carbonation reactor (6), followed by gas sensors for analyzing H<sub>2</sub>S (7) and CO<sub>2</sub> (8).



Figure 5.2: Image of the experimental lab scale set up for combined removal process designed and installed at University Duisburg Essen (Rajavelu 2016).

The gas exiting the carbonation reactor is then finally passed to the exhaust (9). The mass balance for CO<sub>2</sub> uptake was calculated using gas analysis by considering the CO<sub>2</sub> concentration (vol %) at the inlet and outlet of the carbonation reactor column. The H<sub>2</sub>S removal efficiency of the biotrickling filter was determined by analyzing the H<sub>2</sub>S gas concentration (ppm<sub>v</sub>) at the inlet and outlet of the biotrickling filter column. Figure 5.2 shows the laboratory experimental set up for the combined removal process.

To determine overall removal efficiency of the combined removal process, the difference in gas concentration of H<sub>2</sub>S (ppm) and CO<sub>2</sub> (vol %), at the beginning and the

end of the process was calculated. At customary conditions, the gas flow through the bottom ash carbonation reactor is bypassed by nitrogen supply.

Among the tested conditions for H<sub>2</sub>S removal, the previously used biofiltration system that operated with a minimal mass loading rate of 14.285 g S - H<sub>2</sub>S m<sup>-3</sup>.h<sup>-1</sup> was kept constant during the entire combined operations. Under these conditions, the H<sub>2</sub>S removal efficiency was higher than 90 %. For bottom ash carbonation experiments, the lab-scale tests with L/S ratio of 0.1 were selected. The operating conditions for the lab scale combined of H<sub>2</sub>S and CO<sub>2</sub> removal are given in table 5.1.

Table 5-1: Parameters and operating values for lab scale combined removal process

Parameters	Operating values
Gas flow rate (l/h)	20
pH of H <sub>2</sub> S bio trickling reactor	3.2
Temperature of the H <sub>2</sub> S bio trickling reactor (°C)	25.8
Carbonate supply	yes
Mass of bottom ash (g)	423.5
L/S (Liquid/Solid ratio)	0.1
Experimental duration (hrs)	1.5
CO <sub>2</sub> in [vol %]	99
H <sub>2</sub> S in [ppm]	1,000

## 5.2 Pilot-scale material and methods

To test the technical feasibility at a real scale, the integrated system for H<sub>2</sub>S and CO<sub>2</sub> removal was investigated at Leppe landfill site: Metabolon at Engelskirchen, Germany. Landfill site: metabolon is a cooperative project of the waste management organization Bergischer Abfallwirtschaftsverband (BAV) and Cologne University of Applied Sciences, Gummersbach. It was first established in 2010, following the closure of Leppe landfill in 2006.

The most significant combined combustion and compost plant in Metabolon consist of industrial biogas production plant that treats the organic fraction of municipal solid waste (MSW) generated from more than 550,000 inhabitants. The biogas plant consists of twin digesters and a gas storage system. The daily through the output of organic

waste handled is approx 150-200 t/d with a fluctuation organic dry matter content input of 60 % DM and output around 40-50 % DM. The average hydraulic retention time (HRT) is 19 days. Under mesophilic conditions, the concentration of CH<sub>4</sub> in produced biogas varies around 52 to 70 %. The gas is combusted in combined heat and power unit (CHP) that produces 8,000,000 KWh of electrical energy out of 42,000t of oMSW. Among the waste handled, 55,000 tons of biowaste from the domestic biowaste bins and of approx. 5,000 tons of green waste per year is fermentation and composted.

The combined H<sub>2</sub>S and CO<sub>2</sub> removal process experimental set up used at lab scale in University Duisburg-Essen was transported to the Iepe landfill site: Metabolon. The integrated process setup consisting of two units namely (biological desulphurization and carbonation using bottom ash) was housed in a shipping container and placed in between the secondary digester and CHP unit of the Metabolon biogas plant. The gas from the storage tank was extracted using the pipeline as shown in figure 5.3 and directed to the combined removal process unit placed inside the container. The pressure of the gas was around 10- 40 mbar. The exit of the gas after passing through the combined removal process unit was always directed to the outer atmosphere through exhaust pipeline. The gas extracted from the gas collection point is first fed to the biotrickling filtration system. The gas flow entering this system was controlled by Mass flow controller from Bronkhorst GmbH, Germany. The gas flow range was between 10 to 100 l/h and was controlled automatically using flow DDE program on the computer. Figure 5.3 shows the image of the experimental setup that was placed inside the container.



Figure 5.3: Image of the experimental set up for the combined  $\text{H}_2\text{S}$  and  $\text{CO}_2$  removal process installed at Leppe Landfill site: Metabolon, Cologne, Germany (Rajavelu 2016).

The biotrickling filter was freshly inoculated with sulfur-oxidizing bacteria (SOB) obtained from desulphurization tower in biogas anlage, Lunen Germany. The inoculum was diluted with the nutrient solution with 1:1 ratio. The contents of the nutrient solution were described in section 3.1 of chapter 3. The inoculum was recirculated along the packed bed for two days without any gas feeding. Parameters such as pH, dissolved oxygen, temperature and redox potential were monitored continually using automated iks software. A detailed description of biotrickling filtration system used in described in chapter 3.

The gas exiting the biotrickling filtration system was directly fed to the bottom of carbonation reactor containing bottom ash. There is no flow adjustment at this stage. The carbonation reactor is designed to hold 1 kg mass of bottom ash and was designed

using plexiglass. The reactor can be opened from the top for loading and unloading of bottom ash. The bottom of the reactor has a perforated plate to ensure equal distribution of gas flowing through the bottom ash in the packed bed column of the reactor. The reactor is thermally insulated using insulating sheets



Figure 5.4: Location of Leppe landfill site: Metabolon, Cologne Germany adopted from Metabolon entrance poster; Picture at the right shows the biogas collection point from where sample biogas is drawn off for experimental purpose.(Rajavelu 2016).

This is to make sure that the bottom ash is free of any void space that contains unwanted oxygen. The supply of biogas flow is resumed when the oxygen at the outlet gas sensors is lower than 0.2 vol %. Various operation modes can be performed by adjusting shut off valves amongst the gas supply pipelines to run either with biogas or purging with nitrogen

### 5.3 Analytical Methods

Input and output gas flow rates to/from the biotrickling filter and to/from carbonation reactor are measured using Extox ET-8D control unit system. The control unit was upgraded to attach extra transmitters for measuring within the integrated system as shown in figure 5.5. The two transmitters namely CO<sub>2</sub>-100-IR4 for CO<sub>2</sub> gas and H<sub>2</sub>S-100-EC BIO for measuring H<sub>2</sub>S in the range of 0 -100 ppm was installed. It is worth to mention that the H<sub>2</sub>S sensor (H<sub>2</sub>S-100-EC BIO) is mainly used for measuring biogas samples above Hydrogen Sulphide concentrations end value of measuring range up to appr. 500 ppm Temperature range is between - 40 °C to +45 °C and the response Time  $t_{90}$  is the 60 s. Measuring range for CO<sub>2</sub> transmitter is 0 - 100 % (v/v) with response time  $t_{90}$  in 25 s. Figure 5.4 shows the location was biogas was collected.

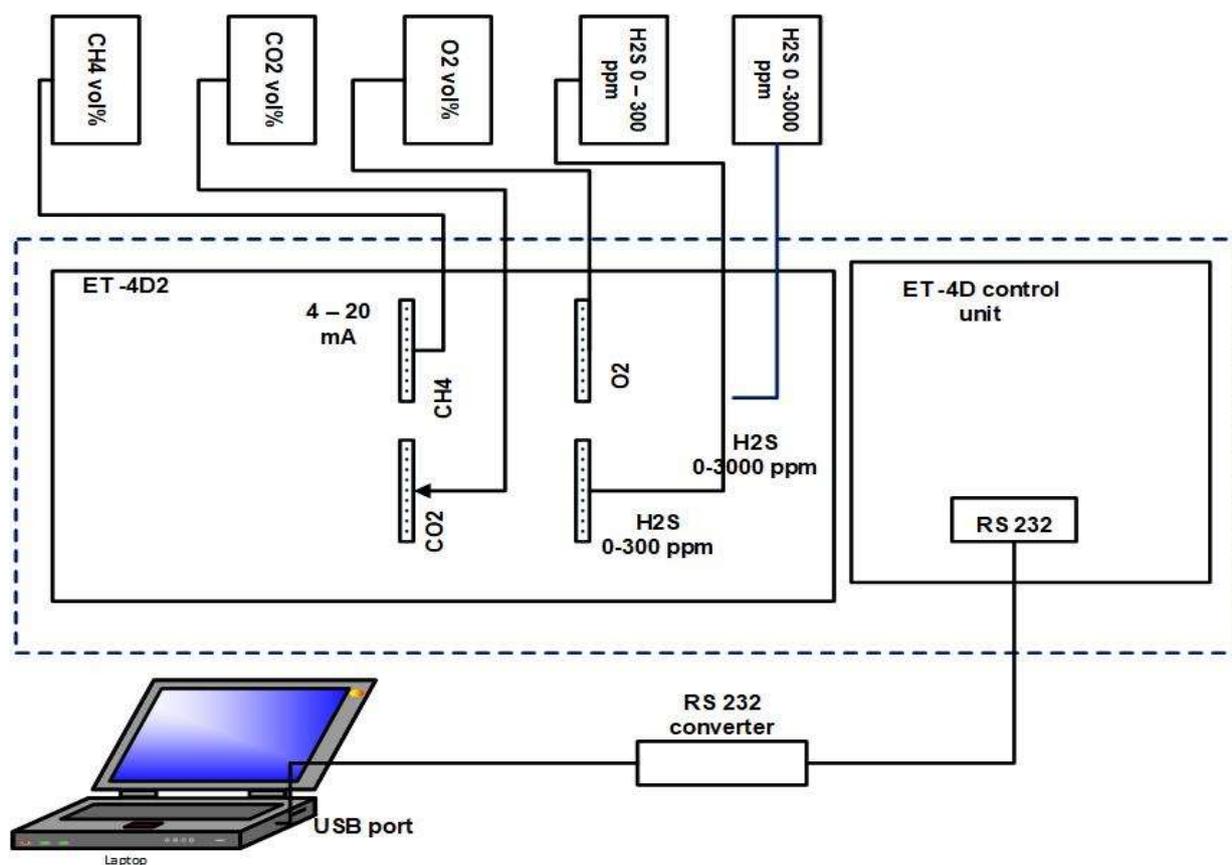


Figure 5.5: Modified ET-8D gas analyzer system for pilot test study conducted at Metabolon, Germany. Sensors for biogas containing  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$  (0-100 ppm),(0 -3000 ppm) are connected to the ET-8D controller from where the measurements are recorded continuously in the computer using RS 232 midibus

For  $\text{CH}_4$  gas measurement, an Infrared sensor named BG-100-IR4 transmitter with a measuring range 0 -100 % (v/v) was used. Working temperature ranges between  $-20^\circ\text{C}$  to  $+55^\circ\text{C}$  and response time  $t_{90}$  was in the 30s. Differential pressure from input and output gas streams was continuously monitored using pressure transducer model PX119 – 100GI (Omega parts, Germany). Measurement from gas sensors or the transmitter-outputs (4-20 mA) were continuously logged into the ET-8D-controller unit and stored in a computer via RS232 using “Terminal.exe” data logger. The ambient temperature was also recorded in the ET-8D-control unit. The pH of bottom ash was tested before and after carbonation in each experimental trial. The pH measurement for bottom ash samples was similar to the description given in section 4.2.2 of chapter 4

For liquid analysis in bio trickling filtration system, the pH value was measured in the recirculation column using iks glass electrode. The data for pH, temperature, redox potential and dissolved oxygen were stored automatically using iks software. The

recirculating liquid was analyzed for the degraded product sulfate. The liquid sample was drawn off from bio trickling filter for sulfate analysis. The sulfate content was determined every 20 minutes using a turbidometric method which was described in chapter 3. The measurement duration is based on the table 5-2 given below.

Table 5-2: Sampling point and sampling measurements for pilot test study

Measured parameters	Unit	Sampling point	Measurement duration
CH <sub>4</sub>	Vol %	Raw gas before CRP; gas after CRP	Every 30s
CO <sub>2</sub>	Vol %	Raw gas; gas after BTF; gas after CR	Every 25s
O <sub>2</sub>	Vol %	Raw gas; gas after CRP	Every 20s
H <sub>2</sub> S	ppm	Raw gas; gas after BTF; gas after CR	Every 60s
Gas quantity	L/h	Gas supply pipeline	Continuous
pH in recirculation BTF		Recirculation point	Every 10 mins
Temperature	°C	Raw gas; gas after CRP; liquid in BTF	Every 15 mins
Dissolved oxygen	mg/l	Recirculation BTF	Every 20 mins

CRP – Combined removal process

BTF - Biotrickling filter

CR – Carbonation reactor (using bottom ash)

Various precautions and safety measures were undertaken to prevent unfavorable circumstances during the experiments at Metabolon. The combined removal process unit was modified to facilitate the incoming biogas with high moisture content. The existing condensate trap was replaced with a higher capacity module to prevent excess humification of the gas handled. The gas always passed through the flame arrestor initially before passing through the integrated combined removal process system. The control unit for the gas detection system has an inbuilt alarm system with LED if the concentration of the gas is exceeding a reasonable value. Safety measures is a must and essential criteria while performing such experiments on a real scale. The experimental rig was placed inside the shipping container situated on the zone 1 area of the metabolon Landfill site. Even though the biogas plant had full safety and equipped function, there are possibilities that biogas can cause an explosion. Methane content determines the proportions. Section 5.4 describes the explosion risk calculation for this experimental purpose.

#### 5.4 Hypothetical explosion risk calculation for biogas during operation of test experiment at Metabolon site, Am Berkebach 1 51789 Lindlar

Table 5-3: Typical biogas concentration from the digesters operated at Metabolon landfill site

Biogas concentration	Vol %
Methane CH <sub>4</sub>	55
Carbon dioxide CO <sub>2</sub>	36
Hydrogen Sulphide H <sub>2</sub> S	0.06
Oxygen O <sub>2</sub>	2
Moisture H <sub>2</sub> O	7.5

Volume of biogas at the inlet = 20 l/h = 480 l/d = 0.48 m<sup>3</sup>/d

Volume of the shipping container (l\*b\*h) = 27 m<sup>3</sup> (approximately)

##### The volume of biogas emitted per day

Methane = 20 l/h \* 55 /100 = 11 l/h = 0.264 m<sup>3</sup>/d

Carbon dioxide = 20 l/h \* 36/100 = 7.2 l/h = 0.172 m<sup>3</sup>/d

Hydrogen sulphide = 20 l/h \* 0.06/100 = 0.000288 m<sup>3</sup>/d

Oxygen = 20 l/h \* 0.2/100 = 0.4 l/h = 0.0096 m<sup>3</sup>/d

Moisture H<sub>2</sub>O = 20 l/h \* 7.5/100 = 0.036 m<sup>3</sup>/d (condensate trap needed for this volume)

##### Explosion risk calculation:

##### Explosion risk for Methane = LEL to UEL= 4.4 % - 16.5 % vol

Amount of methane required for explosion if LEL is 4.4 % = 27\*4.4/100 = 1.188 m<sup>3</sup>

Methane emitted per day in closed room = 0.264 m<sup>3</sup>

The time required for the critical explosion in a closed room approximately= 108 hrs (4.5 days if no ventilation is provided)

##### Explosion risk for biogas = LEL to UEL = 6 % - 22 % vol

Amount of biogas required for explosion if LEL is 6 % = 27 m<sup>3</sup>\* 6/100 = 1.62 m<sup>3</sup>

Biogas emitted per day in closed room during experimental purpose = 0.48 m<sup>3</sup>

The time required for the critical explosion in a closed shipping container = 3.3 days (approximately)

When mixed with air, the Lower explosion limit (LEL) is 5.4 %, and the Upper explosion limit is 16.5 % on volume basis. Below the LEL, there is too little methane to cause an explosion, and beyond UEL, there is too little oxygen which could result in an explosion. Thus for biogas which contains 60 %methane, LEL is 9 %, and UEL is 23 % the temperature needed to cause an explosion is about 650-700 C. At such high temperatures, any spark or the lighted match will be sufficiently hot to cause an explosion. However, this is a risk only when leakage occurs in a tightly enclosed space. Proper ventilation should be provided for biogas to get diluted with air. The shipping container was provided with constant ventilation. A possible explosion risk assessment was made before performing such experiments in explosion zone 1 area of metabolon were the combined removal process unit was installed. The shipping container was equipped with exhaust which operated continuously while the gas supply was on. A safety protocol was prepared by DIN Standards as described below

## 5.5 Results

### 5.5.1 Experimental result from lab scale

The main idea of implementing the combined removal process is to see its feasibility in the removal of contaminants from biogas. Such process will give an idea of how effectively a combined removal process can be operated in a biogas upgrading facility. The study excluded the addition of  $\text{CH}_4$  in the gas mixture as  $\text{CH}_4$  is mainly unreactive and the possible growth of methanotrophic bacteria could affect the overall results. The results from lab scale showed that combined removal process operated well and maintained a stable operation over a prolonged period. Figure 5.6 shows the results of  $\text{H}_2\text{S}$  removal without the addition of the  $\text{NaHCO}_3$  supply. Sulfur-oxidizing bacteria present in the biotrickling filter utilized  $\text{CO}_2$  present in the biogas. It is interesting to note that the autotrophic sulfur-oxidizing bacteria utilize  $\text{CO}_2$  from the air as a carbon source

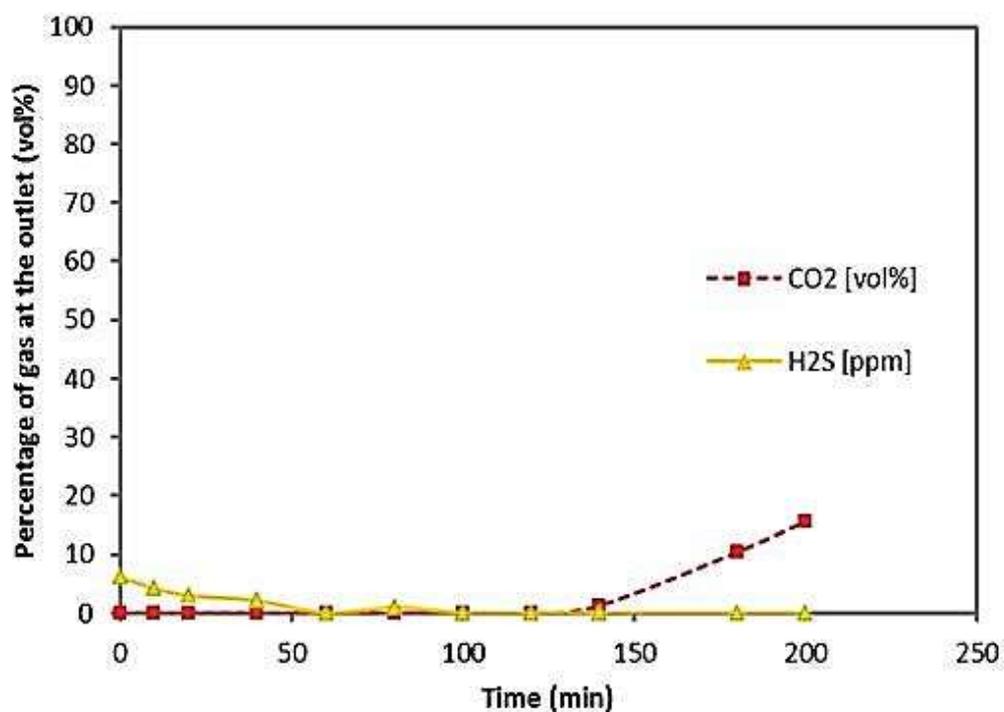


Figure 5.6: Graph showing percentage of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  versus time (mins) at lab scale study.  $\text{H}_2\text{S}$  concentration remained well below 2 ppm for a longer time.  $\text{CO}_2$  concentration started to increase few mins thus showing the breakthrough curve

FISH pictures in chapter 3 confirmed this as the stable population of the sulfur-oxidizing bacterial community was observed both in the presence of  $\text{NaHCO}_3$  supply and  $\text{CO}_2$  enriched biogas supply. Autotrophic bacteria do not emit  $\text{CO}_2$  like heterotrophic bacteria (Jin, Veiga, and Kennes, 2005). Thus the ability to compete in the different  $\text{CO}_2$  environment makes them attractive in robust industrial operations. Though biological removal of  $\text{H}_2\text{S}$  was a continuous process, bottom ash absorption of  $\text{CO}_2$  was a discontinuous batch process with loading and unloading of bottom ash. Albeit, the combined removal process can still be kept continuous by alternative loading and unloading of bottom ash in twin reactors, a substantially conventional practice in similar biogas upgrading process such as PSA, water scrubbing, etc. It is important to note that the removal efficiency decreased during high loading rate of  $\text{H}_2\text{S}$ . This is due to the extreme high  $\text{H}_2\text{S}$  concentration with a relatively less EBRT (s). In such case, the outlet  $\text{H}_2\text{S}$  concentration was found to be higher than 45 ppm. However, this was not found in the combined removal process as the bottom ash also could absorb  $\text{H}_2\text{S}$ . Thus the outlet  $\text{H}_2\text{S}$  concentration remained less than 3 ppm (Figure 6). Similar results were found by (Fontseré Obis *et al.*, 2017). This is interesting especially in sulfur handling capacity of  $\text{H}_2\text{S}$  cleaning technologies. Though the operational cost of a bio trickling filter is less, its capacity of handling sulfur per day is between (8- 450 g/day) as compared to chemical scrubbers that can handle (135-15,000 g of S/day) (Cano *et al.*, 2016). This reduces the choice of using biotrickling filter operation in industries when sulfur-rich biowaste is handled. Thus, coupling biotrickling filter for  $\text{H}_2\text{S}$  removal with bottom ash carbonation will complement the sulfur handling in the biotrickling filter. Thus, removal of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in this combined process could be mutually beneficial when operated in simultaneously. However, this combined removal process could lead to more insight when operated with real biogas conditions at a larger scale.

### 5.5.2 Experimental results from Metabolon landfill site

Various tests were performed with combined removal process by varying the parameters from individual  $\text{H}_2\text{S}$  desulphurization, and  $\text{CO}_2$  carbonation using bottom ash operated serially. Each test was started by flowing biogas from digester through the reactors into combined removal process. In the first step, the biogas enters the desulphurization column. The bio trickling filter containing the sulfur-oxidizing bacterial inoculum is recirculated continuously while the biogas flows into the column. Preliminary results obtained from the lab scale tests allowed to select and fix the following parameters for the biotrickling filter; pH = 2, residence time = 250 s. The gas then flows through the carbonation reactor that is connected serially to the biotrickling filtration system.

The amount of bottom ash in the reactor was kept constant at 500 kg. The bottom ash is replaced once the outlet biogas  $\text{CO}_2$  concentration reaches 5 vol %. After the

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replacement, the biogas pass through the combined removal process is resumed. Several tests were performed to achieve a higher CH<sub>4</sub> concentration at the outlet. The biogas inlet concentration did not vary much, thus allowed to interpret the results directly. Table 5-4 reports the operating conditions and inputs employed in the combined removal process. For tests (1, 2, 3 and 7, 8, 9) carbonate supply was not given to the biotrickling filter allowing the sulfide-oxidizing bacteria to exploit the CO<sub>2</sub> already present in the biogas.

The studies conducted using bottom ash by Mostbauer et al., (2014) was confirmed in the present work under practical conditions. It was noticed that the combined removal process could operate simultaneously thereby achieving a CH<sub>4</sub> concentration of 91.1 vol % at the outlet. Table 5-4 shows the tests conducted at Metabolon (M1, to M9) and the operating conditions and results. The highest concentration of methane was obtained for test M5 with the operating conditions. In general, high CH<sub>4</sub> maxima were obtained in every test. Figure 5.7 shows the composition of the upgraded biogas over a series of time. As soon as the biogas flow was started, there was a decrease in CO<sub>2</sub> concentration. The concentration of CO<sub>2</sub> remained well below 2 % until breakthrough occurs.

When CO<sub>2</sub> is removed, its relative density is decreased thereby increasing the CH<sub>4</sub> concentration at the outlet. In practice, separation of CO<sub>2</sub> and CH<sub>4</sub> from gaseous mixture entails various operational parameters. The perspective of designing this combining removal system is to predict the changes in the CH<sub>4</sub> concentration at the outlet concerning changes within the system.

Each component in the system may present different resistances such as pressure drop and gas flow rates etc. It is to be noted that the outlet CH<sub>4</sub> concentration does not meet the biomethane standard of (> 96 % purity). The CH<sub>4</sub>/CO<sub>2</sub> selectivity in membrane upgrading systems offers a relatively low selectivity which results in 10 % to 25 % methane loss in single stage configurations. Thus membrane systems are efficient only when used multistage.

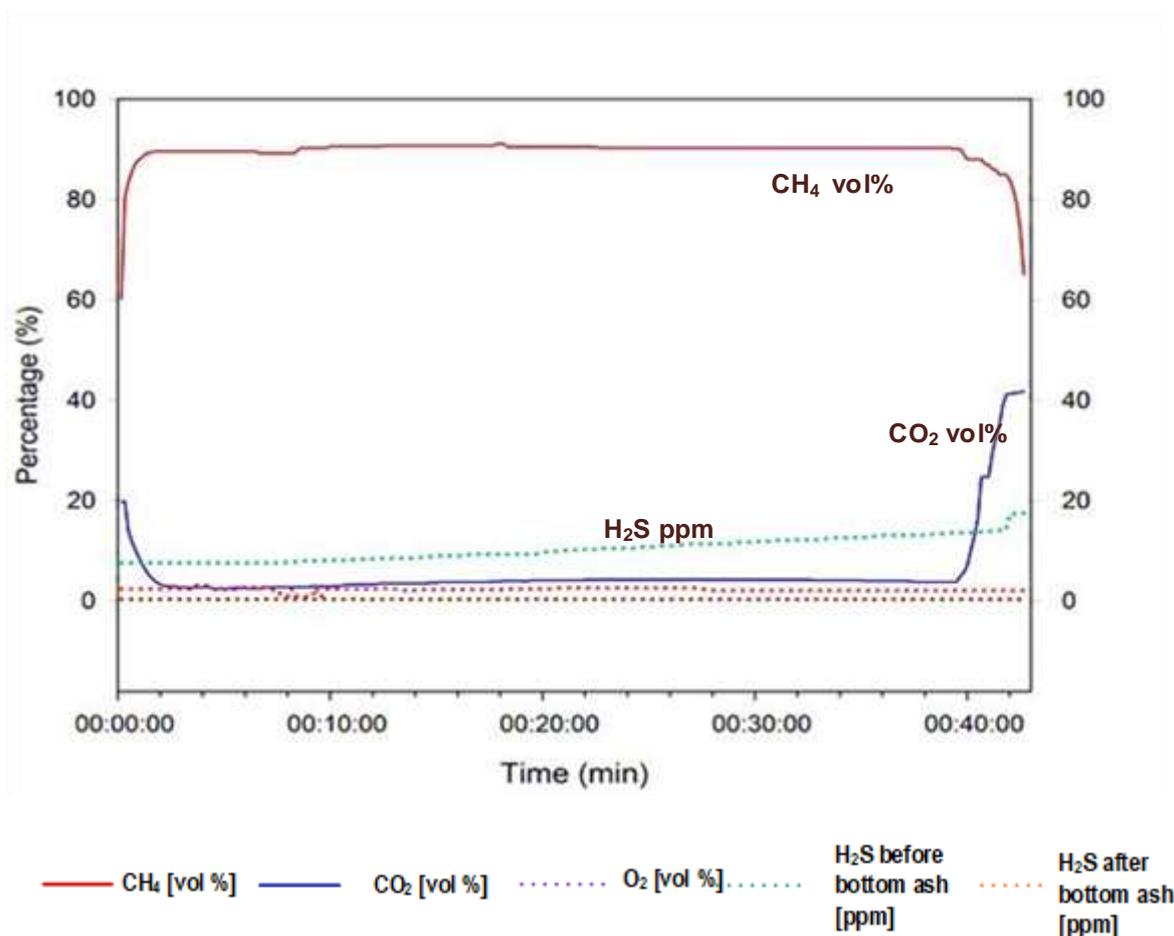


Figure 5.7: Variations in the biogas concentration as a function of time (mins). The CH<sub>4</sub> concentration in biogas started to increase as soon as the gas flow is initiated. CO<sub>2</sub> concentration remained zero (vol %) until the breakthrough point is reached. O<sub>2</sub> remained zero throughout the process. H<sub>2</sub>S concentration in biogas remained below 20 ppm before passing into bottom ash reactor. The H<sub>2</sub>S concentration in biogas after passing into bottom ash reactor remained below 5 ppm.

The low methane concentration at the outlet of the combined process could be enhanced when used with multi-stage upgrading system. However, the CH<sub>4</sub> volumetric content of 90 % does not necessarily correspond to the absence of CO<sub>2</sub> in the biogas. This may be due to the presence of other gas impurities such as oxygen, nitrogen, and H<sub>2</sub> in the system. However, this does not majorly affect the combined process feasibility on a real scale. This is of concern with the biogas upgrading technology due to the possible dilution of biogas with oxygen and nitrogen. Nevertheless, use of activated carbon filters could absorb the excess nitrogen and oxygen from the system as in all

other upgrading technologies. Figure 5.8 shows the differences in H<sub>2</sub>S concentration before and after passing onto the bottom ash reactor.

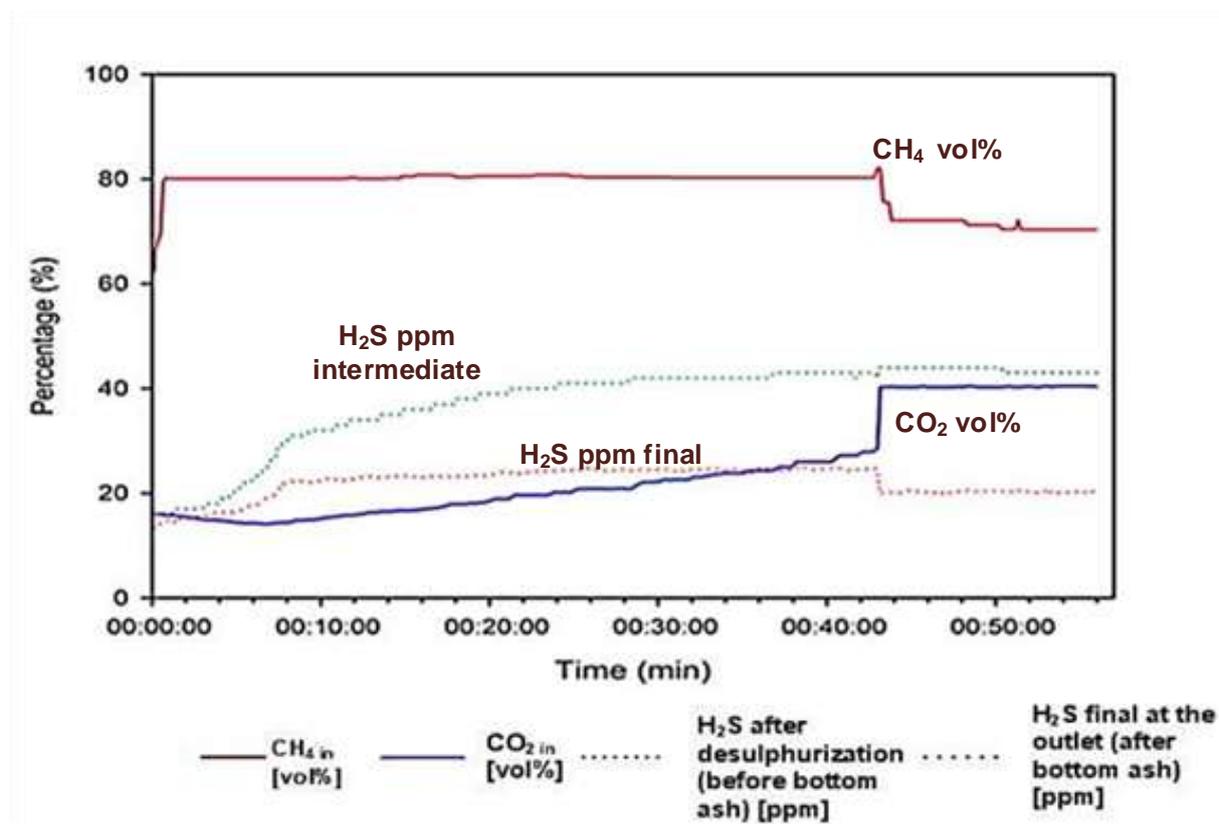


Figure 5.8: Experimental result from test M9 showing the difference in H<sub>2</sub>S concentration before and after passing onto the bottom ash reactor. There is definite evidence that H<sub>2</sub>S concentration at the outlet remained well below <4 ppmv after passing through bottom ash indicating that bottom ash adsorption of H<sub>2</sub>S has taken place.

There is definite evidence that H<sub>2</sub>S concentration at the outlet remained well below <4 ppmv after passing through bottom ash indicating that bottom ash adsorption of H<sub>2</sub>S has taken place. It is of worth to mention that under proper process parameters, the CH<sub>4</sub> volumetric content of 96 % to 99 % is achievable using bottom ash upgrading (Mostbauer *et al.*, 2012). Oxygen is another essential contaminant which is to be removed. Use of aerobic desulphurization process may result in higher oxygen content in the biomethane gas stream. However, use of oxygen diffusion in recirculation liquid in this present work helped to achieve almost zero percentage of oxygen at the outlet. The CO<sub>2</sub> uptake capacity remained the same between 10.2 -14.56 g CO<sub>2</sub>.kg<sup>-1</sup>

Table 5-4 Results from experimental trials conducted at metabolon landfill sites

Experiment	M1	M2	M3	M4	M5	M6	M7	M8	M9
Biogas flow rate (L/h)	20	20	20	20	20	20	20	20	20
Aerobic desulphurization	Yes								
pH of H <sub>2</sub> S bio trickling reactor	2.1	2.3	2.7	2.1	3.4	3.1	1.5	2.4	3.8
Temperature of the H <sub>2</sub> S bio trickling reactor (°C)	23.1	28.8	28.3	11.6	28.9	24.7	26.5	28.9	23.5
Carbonate supply	No	No	No	No	Yes	Yes	No	No	No
Mass of bottom ash (g)	400	400	400	400	400	400	400	400	400
L/S (Liquid/Solid ratio)	0.05	1.0	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Experimental duration (hrs)	1.5	2.4	1.5	2.0	1.5	2.8	2.0	1.5	1.5
CH <sub>4</sub> <sub>in</sub> [vol %]	58.1	55.7	54.3	57.2	53.8	54.5	58.2	49.8	58.2
CO <sub>2</sub> <sub>in</sub> [vol %]	40.9	40.4	39.6	40.9	42.5	41	40.9	36.9	40.8
H <sub>2</sub> S <sub>in</sub> [ppm]	383	579	428	422	608	369	381	377	467
CO <sub>2</sub> breakthrough time (min)	42	40	41	42	-	45	48	52	-
H <sub>2</sub> S after desulphurization (before bottom ash) [ppm]	79.6	61.3	75.8	70.8	45.8	41.0	93.0	67.9	46.0
H <sub>2</sub> S final at the outlet (after bottom ash) [ppm]	<3	<3	1.5	<4	1.6	2	<4	<3	<4
Temperature gas in (°C)	21.7	23.1	25.6	24.4	21.1	19.8	17.5	18.9	19.1
Temperature gas out (°C)	28.2	26.7	29.1	27.3	28.9	25.7	24.6	24.1	28.9
CH <sub>4</sub> <sub>out</sub> [vol %]	88.9	90.4	90.7	90.6	91.1	78	86.4	88.7	87.5
CO <sub>2</sub> <sub>out</sub> [vol %]	0	0	0	0	0	0	0	0	0

## 6 Life cycle Assessment (LCA) and Techno-Economic Analysis for the combined removal process for biogas upgrading

### 6.1 Introduction to Lifecycle Assessment (LCA)

The purpose of conducting a life cycle assessment (LCA) was to understand the environmental impact of the combined removal process in upgrading biogas. The analysis is carried out under the methodological framework of LCA created by the International standards organization (ISO 14040:2006). Life cycle assessment by definition is the compilation and evaluation of inputs and outputs entering and leaving the product system. This accounts for all the impact categories that affect the environment directly or indirectly. There are two LCA standards created by International standard organization. ISO 14040 and ISO 14044. There are several types of LCA usually conducted within the framework such as cradle to gate model, gate to gate model, gate to grave model, cradle to grave model and cradle to cradle model. This chapter focuses on cradle to gate model in which the biogas produced is upgraded using combined removal process for further use. Performing LCA of one product or process is not relevant.

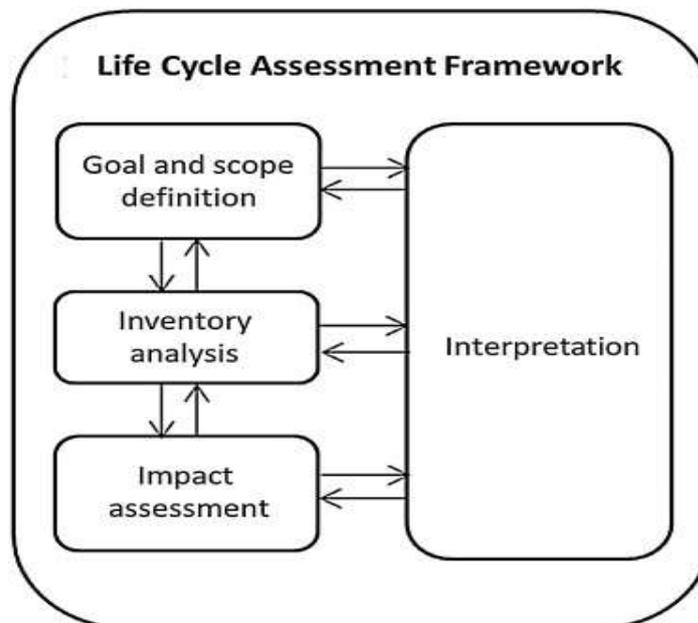


Figure 6.1: Four significant steps of Life cycle assessment and the interrelation. (ISO 14040:2006)

It is quintessential to compare various processes of a similar process to understand in-depth the pros and cons of the current developed design. LCA has four significant steps namely 1) goal and scope definition 2) Inventory analysis 3) Impact assessment phase 4) Interpretation of results. These steps are essential in carrying out the assessment and interpreting the results as shown in figure 6.1.

The following environmental and energy analysis for combined removal process using the methodological framework of LCA was carried using “cradle to gate” approach (DIN EN ISO, 2006). Many LCA has already been suggested in the literature for CO<sub>2</sub> removal methods, but such analysis has often ignored H<sub>2</sub>S removal step in biogas upgrading process. To our knowledge, this is the first time LCA is conducted for both H<sub>2</sub>S removal and CO<sub>2</sub> removal process in biogas upgrading stage.

### **6.1.1 Goal and scope definition**

The goal and scope of this study were based on ISO 14040 guidelines. The intended application of this entire LCA study was to evaluate the environmental impact in upgrading biogas to biomethane using combined H<sub>2</sub>S and CO<sub>2</sub> removal process. The functional unit considered is the production of one kWh of biomethane from internal combustion engine as per in compliance with the LCA method. The environmental impact associated with the emission of one kWh of biomethane was calculated using CML (Centrum voor Milieukunde Leiden) method, described by (Guinée, 2002)

The scope of this study included a scenario of investigated upgrading process at a biogas plant situated near a landfill site. This scenario model mimics the metabolon landfill site located in Engelskirchen, Germany where a biogas plant is located nearby the landfill site separated by a distance less than 5 km. Hence the location of the modeled system is in Germany as a consequence of climate data referring to Germany. The intended LCA study included only the total amount of reagent used for combined H<sub>2</sub>S and CO<sub>2</sub> removal process, energy and transport required for the process

### **6.1.2 Inventory Analysis and Assumptions**

The inventory analysis is the compilation of all the inputs (mass flow, energy flow, etc) and outputs (products, co-products, waste generated, etc) for the given product system in its entire life cycle flow or single process flow. The Lifecycle inventory (LCI) for the combined H<sub>2</sub>S and CO<sub>2</sub> removal process was collected based on the figures derived from literature and communication with the industrial partners. The figure 6.2 below shows the overview of the system boundary studied for LCA for combined removal process for biogas upgrading. The process investigated requires electrical energy supply invariably which is obtained from Germany (DE) national grid. Gabi software 4.0 for LCA with databases (IKP, PE, 1992 – 2002) was used for calculations and analytics.

The emission factors associated with the national grid mix from Germany is applied using Ecoinvent database 2.0 (Frischknecht *et al.*, 2007). Biomethane produced at the end of upgrading process is assumed to fit the substitute for natural gas (average CH<sub>4</sub> content 97 %) standards (Persson, Jonsson and Wellinger, 2007). The process flow diagram given in figure 6.2 explains the unit operation of the combined removal process. Biogas produced from anaerobic digester is passed through the system where H<sub>2</sub>S and CO<sub>2</sub> are removed in the combined process.

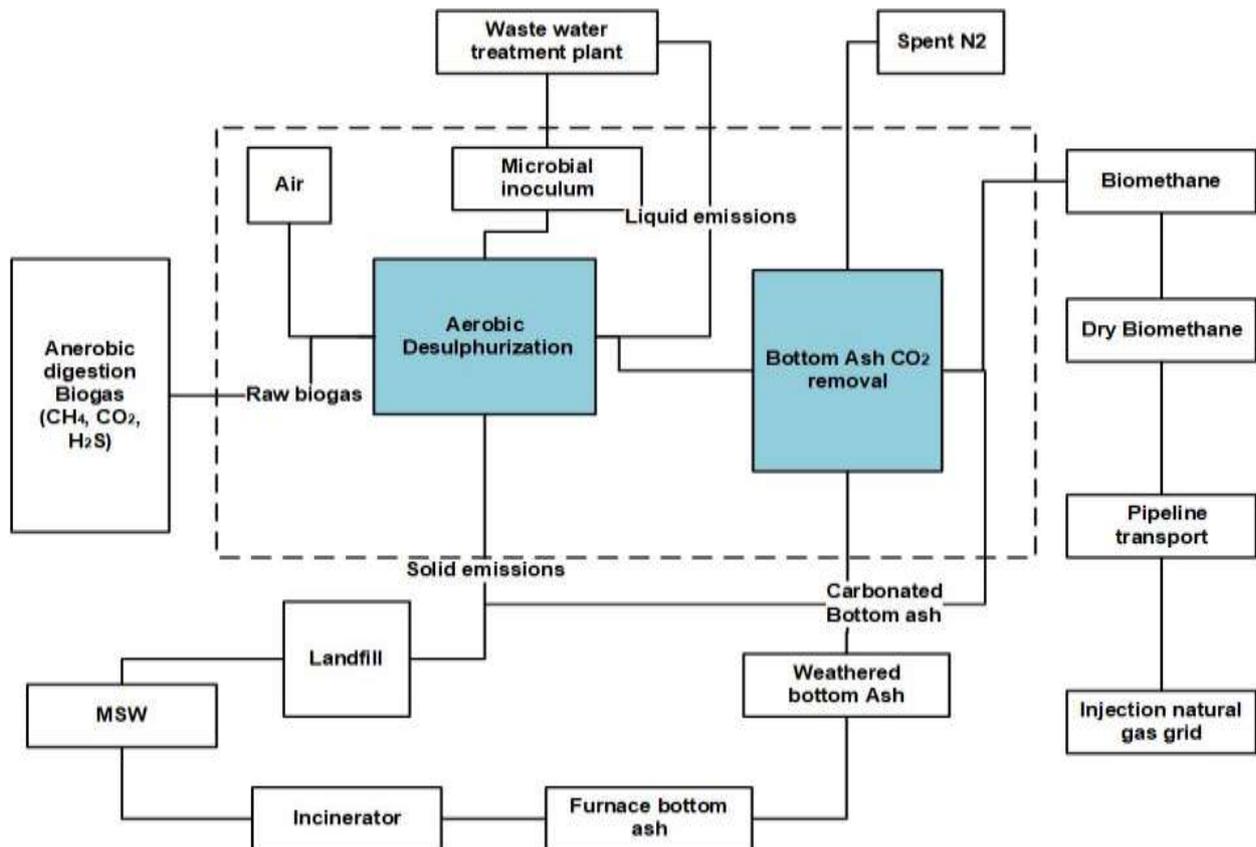


Figure 6.2: Process layout coupling aerobic desulphurization with bottom ash CO<sub>2</sub> capture for LCA study

The biogas produced is assumed to have a theoretical composition 50 % CO<sub>2</sub> and 50 % CH<sub>4</sub> by volume and an H<sub>2</sub>S inlet concentration of 3,000 ppmv. It is first passed through aerobic desulphurization tower which removes H<sub>2</sub>S. The inventory consisting of chemicals, energy supply, and a bacterial source supplied for the necessary removal of H<sub>2</sub>S is included whereas the infrastructure with its auxiliary equipment such as pumps, pipes, etc are excluded from the study. Air is essential for aerobic desulphurization for oxygen supply. The emissions from H<sub>2</sub>S removal in the form of liquid, solid and air is also included in the study. The generated liquid emissions consisting of sulfate and sulfite was sent to the waste treatment plant for further treatment after the solid

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elemental sulfur ( $S^{\circ}$ ) particles are separated for further use. The accumulated biomass as a result of sulfur oxidation is sent to a landfill site.

It has been proven in the above study that is technically feasible to remove 99.9 % of  $H_2S$  from biogas using aerobic desulphurization (see chapter 3). Biogas after passing through aerobic desulphurization reactor is passed through  $CO_2$  removal step using bottom ash (refer to chapter 5). The bottom ash required for the process is transported from the nearby landfill site. The transport distance of 5 km is fixed for the present study assuming the landfill site is nearby the biogas plant. Diesel fuel is required for the truck to transport bottom ash. Truck with a payload of 27t is assumed, and the Ecoinvent 2.0 database was used for calculating emission factors related to diesel fuel that also includes empty return transport. Furnace bottom ash produced by the municipal incineration was selected from Gabi professional database with the object category named waste for recovery. Nitrogen is required for flushing and purging of bottom ash particles after each experimental run and hence added to the LCA study. After upgrading, the biogas undergoes compression and drying based on the process suited for the specific required gas condition. Gas is then passed through pipelines for final energy conversion in a CHP plant. The climate balance includes emissions from biogas upgrading and energy supply necessary for the production of biomethane. Emissions associated with biogas generation such as pretreatment of biomass, anaerobic digestion, landfilling, waste treatment plants, the housing of the system, material for construction of the entire system, infrastructure, transportation of biomethane to the natural gas grid and its combustion in internal combustion system is excluded from the study

## 6.2 Techno-Economic Analysis

Economic assessment for the combined removal process and PSA upgrading with aerobic desulphurization was performed to study the economic feasibility. Renewable energy from biogas in the form of electricity and biomethane fuel has attracted more considerable economic incentives in EU. The most widely used technology for energy conversion in Europe is CHP (Combined heat and power). The CHP does not require biogas upgrading as most of the CHP units are resistant to  $H_2S$  corrosiveness. One of the significant disadvantages of using CHP is the limited efficiency which is typically in the range of 30 – 40 % (Budzianowski, 2016). With the amount of energy required for biogas plant operation ranging from 25 - 50 %, the use of CHP could not be a significant benefit regarding selling excess electricity or heat. Biogas upgrading could be beneficial as the energy efficiency of converting raw biogas to biomethane is usually >97 % for example in PSA (pressure swing adsorption) upgrading plant (Berndt, 2005). Many upgrading technologies are currently viable both technically and economically. It is also blatant that all technologies  $CO_2$  neutral. (i.e., the biogenic  $CO_2$  is still emitted

into the atmosphere). Carbon capture and storage technology (CCS) has proven to play an essential role in decarbonizing the environment. EU climate policy has identified this and has encouraged the technology by various programmes such as Directorate-General for Climate Action (DG CLIMA) and the NER 300 funding programme. This study investigates the performance of combined removal process with its economic viability with the current PSA upgrading technology and CHP unit. This study evaluates the economic constraints and analyses the weak points, as well as the advantage of decarbonization in the combined removal process, could offer in biogas upgrading Industry. Within the current study, three technologies such as Combined heat and power (CHP), PSA upgrading with aerobic desulphurization denoted as (PSA - AD), and combined removal process using bottom ash and aerobic desulphurization denoted as (CRP BA - AD) is explored using techno-economic analysis. Three scenarios for biogas plants such as (CHP, PSA - AD, CRP BA - AD) is chosen for economic analysis to understand how these processes differ regarding energy production as well as cost and support schemes from EU.

### 6.2.1 Technical characteristics and support schemes for three scenarios

Scenario 1 consists of a biogas plant with Combined heat and power generation unit (CHP). The biogas plant processes around 10.4 Kt/a of energy crops with a working volume of the digester in 2,700 m<sup>3</sup> with a hydraulic retention time of 70 days. The plant has a large-scale combined heat and power unit (CHP) unit for power generation. The CHP unit. The gas engine from Clark energy is used as a reference CHP unit of LHV based electrical efficiency of 35 % and remaining 50 % of biogas energy converted to heat and remaining 15 % as losses. The capital investment and the operational cost including CHP unit of a typical biogas plant are found from literature and tabulated in table 6.1. The plant produces excess energy which can be traded using feed-in tariff for electricity. In Germany, the bonus is 8 euro/KWh for feeding renewable electricity according to (*The Renewable Energy Sources Act, 2012*). Scenario 2 consists of biogas plant processing about 19 kt/ an of energy crops thus producing about 400 m<sup>3</sup>/h of raw biogas which is upgraded to biomethane. The upgrading unit consists of biological desulphurization and a pressure swing adsorption unit denoted as PSA - AD in this study. The capital cost, as well as the operational cost for both processes operated, is given in the table below. The produced biogas first passes through biological desulphurization and after that to pressure swing adsorption process. The exiting biomethane has a methane content >97 %. The separated biogenic CO<sub>2</sub> from biogas is let into the atmosphere.

The third investigated scenario is the biogas plant that utilizes combined removal process for biogas upgrading to biomethane. The process described as in chapter 4 consists of aerobic desulphurization process coupled to bottom ash removal process

denoted as CRP BA – AD. Unlike pressure swing adsorption process, the biogenic CO<sub>2</sub> separated from raw biogas is stored within the bottom ash in a mineralized form, thus decarbonizing the whole process. The capital cost, operating cost as well as other annual costs have been calculated from elsewhere for both the processes.

For scenario 2 and 3, there upgraded biomethane can be either sold to the natural gas grid or used as a fuel. The cost of grid usage with natural gas operators is 0.06 euros/kWh. Also, the produced biomethane can be sold as a fuel which will incur an income of 0.09 euros/kWh. There is an avoided network fee which is given as a bonus when the biomethane fed into the gas grid (*GasNZV, 2012*) that has an income of 0.07 euros/kWh

## 6.3 Results

### 6.3.1 Mass and Energy flow consumptions

The mass and energy flow for the production of 1 kWh of biomethane is shown in table 6-2. LCA gives an insight into various pathways where the energy consumption is high and helps us in identifying the weak points. Results of energy and mass balance for the production of 1 kWh of biomethane is shown in table 6-1. The energy breakdown for bottom ash CO<sub>2</sub> capture is 0.017 kWh (Pettersson and Wellinger, 2009) (Lems and Dirkse, 2010) (Starr *et al.*, 2012) and for aerobic desulphurization is 0.016 kWh (Cano *et al.* 2016). The total amount of energy regarding electricity required for the combined removal process required amounts to 0.033 kWh. Raw biogas of 0.203 m<sup>3</sup> is required for producing 1 kWh biomethane. Table 6-1 shows the energy efficiency of the biogas upgrading system using combined removal process and Pressure swing adsorption (PSA) for standard reference.

The amount of air required for aerobic desulphurization amounts to 0.025 kg. Furnace bottom ash is transported from landfill site to the upgrading chamber using truck trailer thus the usage of diesel for transportation amounts to 0.00024 kg. The amount of bottom ash that will be required for producing the functional unit of 1 kWh of biomethane amounts to 8.89 kg. Every step in this upgrading process requires significant energy requirement. The highest impact on all categories comes from the use of electricity mix for upgrading process with an overall impact of 56.8 %.

$$\dot{\eta} = E_{\text{sys produced}} / m_{\text{biogas}} * LHV_i + E_{\text{sys consumed}} \quad 6.1$$

$\dot{\eta}$	plant energy efficiency	
$E_{\text{sys produced}}$	net energy produced from biomethane	kW, m <sub>i</sub>
$m_{\text{biogas}}$	the mass flow rate of raw biogas	m <sup>3</sup> /h

LHV <sub>i</sub>	lower heating value or the calorific value of the raw biogas	KW
E <sub>sys consumed</sub>	the total amount of energy consumed for biogas upgrading process	

This is similar to LCA conducted by Starr *et al.* (2014). However, the overall energy efficiency of combined removal process reached up to 84 % without the use of heat. The energy efficiency of biomethane is calculated using plant energy efficiency index (Dimitriou *et al.*, 2015) and is given in equation 6.1

Table 6-1: Comparison of energy efficiency for combined removal process and PSA in biogas upgrading.

Biogas upgrading pathway	Net energy input (KWh)	Raw biogas (m <sup>3</sup> /h)	LHV of raw biogas	The net energy output of biomethane (kWh)	Plant energy efficiency (%)
Combined removal process	1.251	0.203	6	1.056	84
PSA	1.285	0.203	6	1.056	82

### 6.3.2 Environmental impact and process contribution

The process contribution to environmental impacts for the production of 1 KWh of biomethane is shown in figure 6.3. The CML 2001 impact assessment method was used for this study. The selected environmental impact categories include global warming potential 100years (GWP) [kg CO<sub>2</sub>-Eq]; abiotic depletion elements (ADP E) [kg Sb-Rq]; abiotic depletion fossil (ADP F) MJ; acidification potential (AP) [kg SO<sub>2</sub>-Eq]; eutrophication potential (EP) [kg PO<sub>4</sub>- Eq]; freshwater aquatic ecotoxicity (FAETP) [kg 1,4-DCB-Eq]; human toxicity potential 100 years (HTP) [kg 1,4-DCB-Eq]; marine aquatic ecotoxicity potential (MAETP) [kg DCB -Eq]; ozone depletion potential 40 years, (ODP) [kg CFC-11-Eq]; photochemical oxidation potential (POCP) [kg ethane- Eq]; terrestrial ecotoxicity, 100 years (TAETP) [kg 1,4-DCB-Eq]. Four stages have been analyzed using the impact mentioned above categories, they include

- Electricity grid mix: impacts related to energy consumption which comes from electricity grid mix required by the process;
- Methane loss; impacts associated with methane emission;

- Sulfate emission: impacts related to the aerobic desulphurization liquid emissions that include sulfate;
- Transport: impacts related to the transport of bottom ash from landfill site to the upgrading system.

For most of the impact studied, the electric consumption shows most contribution. The proportion for GWP is 56.8 % whereas, for abiotic depletion fossil and elements and human toxicity, the contribution of electric consumption is more than 80 %. The next higher impact in all categories is caused by transport of bottom ash from landfill site to the biogas upgrading process.

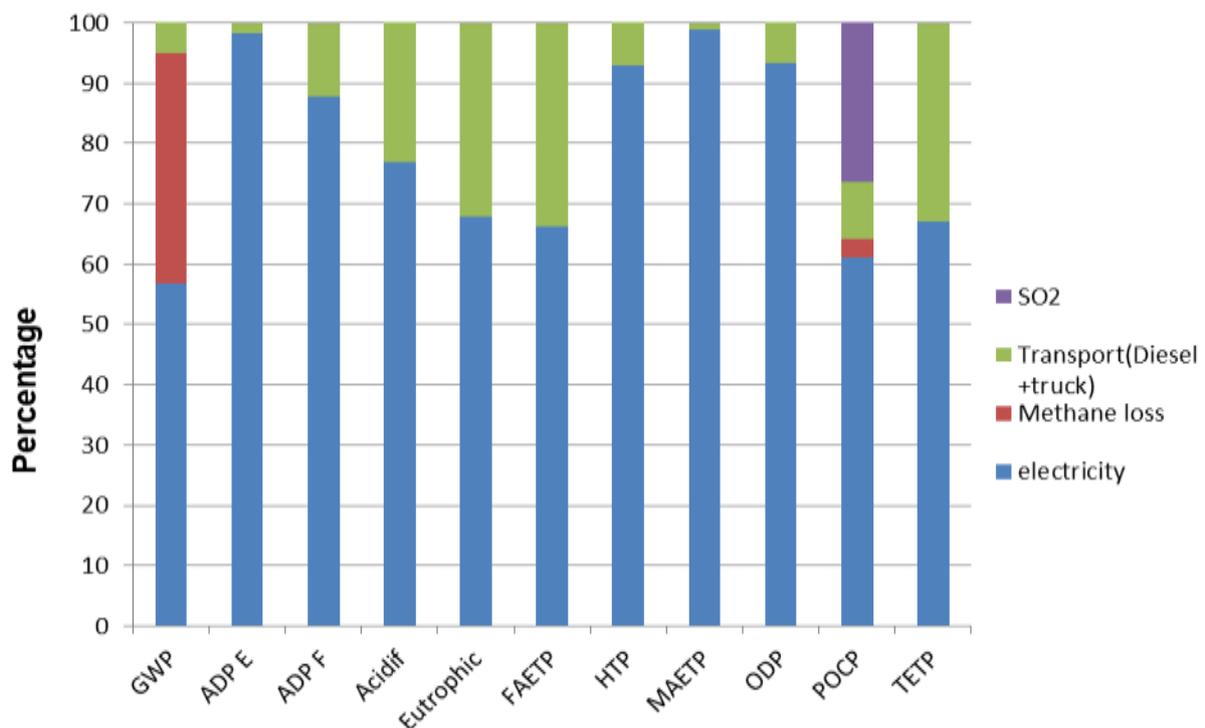


Figure 6.3: Life cycle assessment (LCA) for combined removal process method for biogas upgrading. Simplified LCA showing environmental impact for the studied categories. Global warming potential 100years (GWP) [kg CO<sub>2</sub>-Eq]; abiotic depletion elements (ADP E) [kg Sb-Rq]; abiotic depletion fossil (ADP F) MJ]; acidification potential (AP) [kg SO<sub>2</sub>-Eq]; eutrophication potential (EP) [kg PO<sub>4</sub>-Eq]; freshwater aquatic ecotoxicity (FAETP) [kg 1,4-DCB-Eq]; human toxicity potential 100 years (HTP) [kg 1,4-DCB-Eq]; marine aquatic ecotoxicity potential (MAETP) [kg DCB -Eq]; ozone depletion potential 40 years, (ODP) [kg CFC-11-Eq]; photochemical

oxidation potential (POCP) [kg ethane- Eq]; terrestrial ecotoxicity, 100 years (TAETP) [kg 1,4-DCB-Eq].

The impacts can be found in global warming potential 5.31 %, abiotic depletion 98.3 % eutrophication potential 67.8 % and in freshwater aquatic ecotoxicity 66.3 %, photochemical ozone creation potential 61.1 %. The impact due to the transport is mainly because of the diesel mix used for the truck. However, use of biomethane in place diesel fuel could lead to a more significant advantage in reducing environmental damage. Also, when the distance between the collection and use of bottom ash can be reduced, the environmental impact due to transport can be majorly reduced. Methane loss does cause a significant impact on global warming potential (GWP) with an impact percentage of 38.1 %. Notably, methane loss has a contribution of 3 % in photochemical ozone creation potential. Aerobic desulphurization also causes environmental impact due to the liquid and solid emissions which majorly contain sulfur and sulfate. However, this can be nullified by proper waste treatment.

Table 6-2: Life cycle inventory for the production of 1 kWh of biomethane using combined removal process

Inputs	Bottom ash CO <sub>2</sub> removal	H <sub>2</sub> S desulphurization	References
Electricity (kWh)	0.017	0.016	(Katherine Starr <i>et al.</i> , 2012)
Diesel(Refinery products) (Kg)	0.002		(Frischknecht <i>et al.</i> , 2007)
Furnace bottom ash (kg)	8.89		This work
Microbial wastewater (kg)		4.8	(Cano <i>et al.</i> , 2016)
Air (kg)		0.025	This work
Nitrogen (kg)		0.015	This work
Biogas (m3)	0.203		This work
Methane loss (%)	0.78		(Mostbauer <i>et al.</i> , 2012)
Outputs			
Biomass (kg)		0.011	(Cano <i>et al.</i> , 2016)
SO <sub>4</sub> <sup>-2</sup> (kg) (residue for recycling)		0.001	(Bailón Allegue and Hinge, 2014)

### 6.3.3 Comparison of LCA for combined removal process and Pressure swing adsorption (PSA) and aerobic desulphurization

To better understand the environmental impacts of the studied combined removal process with other upgrading technologies available in the market, a simplified LCA was conducted for Pressure swing adsorption (PSA) technology combined with aerobic desulphurization and combined removal process. The main factors include only electricity consumption, transport and the reagents used for both the process.

Figure 6.5 shows the comparison of all impact categories for both PSA combined with aerobic desulphurization versus combined removal process. In all cases, combined removal process showed least toxicity and impact compared to PSA technology. This is mainly due to the electricity consumption for PSA which is higher compared to the combined removal process. Also, methane loss for PSA upgrading is higher than combined removal process, thus increasing the overall impact. While, electricity, transport, and methane loss contribute to the overall GHG emissions in the combined removal process, electricity consumption alone caused a higher GHG emission in PSA.

It is believed that the impact on marine ecotoxicity potential and freshwater ecotoxicity potential in both technologies is mainly caused due to the use of aerobic desulphurization process. Similar results were ascertained by (Cano *et al.* 2016). However, concerning the global warming potential, the contribution of aerobic desulphurization in both upgrading process was significantly less (0.012 kg CO<sub>2</sub>) making it environmentally favorable process to be in conjunction with either PSA or combined removal process. Overall, all other categories showed more significant impact (>97 %) such as ADPE, ADP F, HTTP, TETP, MAETP, eutrophication potential. It should be noted that combined removal process can capture CO<sub>2</sub> due to bottom ash adsorption thereby reducing the overall impact of global warming potential category. In PSA, the desorption releases CO<sub>2</sub> into the atmosphere. It is also possible to capture CO<sub>2</sub> from the exhaust gas which can be liquefied for further usage. Albeit, there exists a challenge for the purity of CO<sub>2</sub> in exhaust gas stream from PSA for liquefaction. Usually, CO<sub>2</sub> liquefaction required more than 99 % purity (Wetenhall *et al.* 2014) (Lems and Dirkse, 2010) which is possible in membrane upgrading systems but not technically feasible in PSA systems or which may require a higher electricity consumption.

### 6.3.4 Global warming potential and Carbon balance

It is undisputed that biogas upgrading represents the second highest CO<sub>2</sub> emissions in the entire biogas supply chain (Pertl, Mostbauer, and Obersteiner, 2010). To comply with German standard for biomethane injection in natural gas networks, an average

content >96 % should be assumed for the end product biomethane. However, the lab-scale developed combined removal process could reach methane content not higher than 90 %. This is similar to a fully functional upgrading plant such as pressure swing adsorption (PSA) which achieve methane content not higher than 95 % due to high methane losses.

In such cases, it is usual to dose liquid gas such as propane in gas network lines. Apart from meeting the national standards, biomethane plants do suffer methane losses contributing to greenhouse gas emissions (GHG). However, in a study (Urban, 2011), the potential CO<sub>2</sub> emissions (tons of CO<sub>2</sub>-Eq) from various utilization pathways such as biogas CHP, upgrading biogas with CHP utilization, upgrading biogas and injection to the gas grid were analyzed.

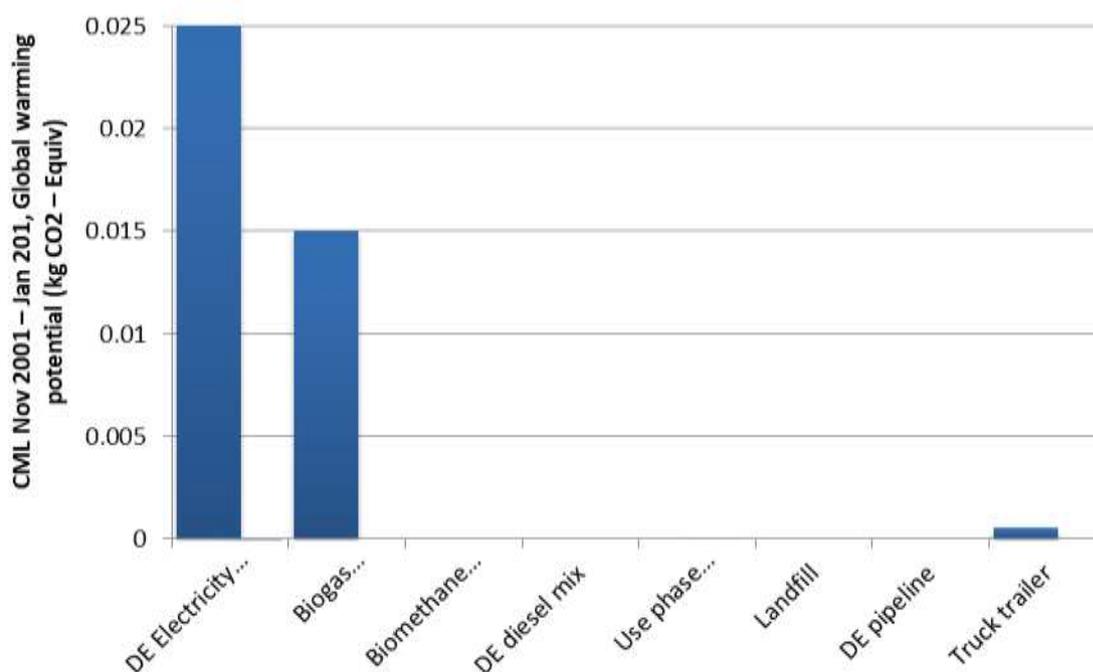


Figure 6.4: Global warming potential (kg CO<sub>2</sub>-Equiv) for the production of 1 kWh biomethane from combined removal process.

Upgrading biogas with CHP usage and 100 % heat recovery showed highest emissions savings (12.7 tons of CO<sub>2</sub>-Eq). With the replacement of biofuel quota by greenhouse gas emission quota (Energien, 2017), it is quintessential to identify the hotspots of CO<sub>2</sub> emissions in the developed combined removal process for biogas upgrading. All emissions including, CH<sub>4</sub>, CO<sub>2</sub> biogenic and non-biogenic is included and are multiplied by their conversion factor for CO<sub>2</sub> equivalents. Results obtained states that significant

GHG emissions from the upgrading process are caused by the use of electricity grid mix. Starr *et al.* (2012) ascertain that all biogas upgrading process contributed a significant amount of GHG emission due to higher consumption of electricity.

In PSA method, a reasonable amount of electricity consumed added to the entire energy consumption. Transport of bottom ash by the use of diesel fuel amounted to 0.0007 kg of CO<sub>2</sub>. Thus the contribution of global warming potential as a result of CO<sub>2</sub> emission equivalent transportation by diesel fuel resulted in only 5.31 % as compared to that of BABIU process which resulted in 18 % GHG emission (Starr, 2013).

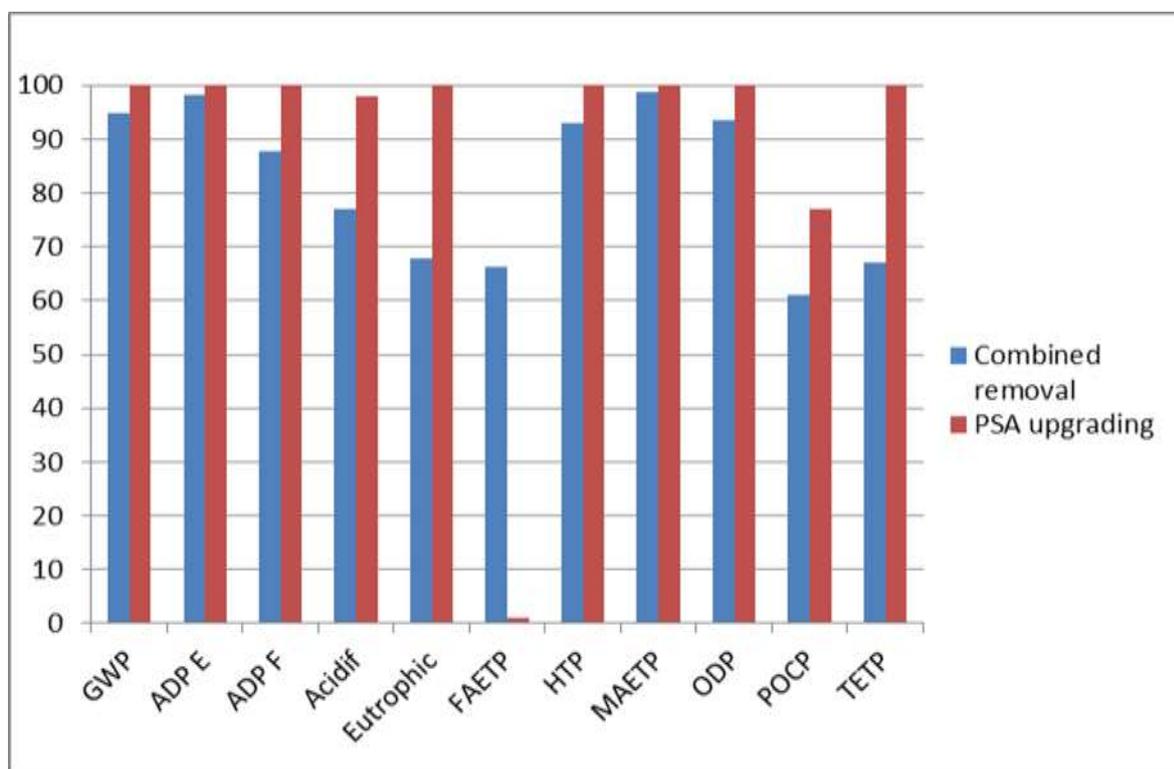


Figure 6.5: Comparison of Life cycle assessment (LCA) for combined removal process and Pressure swing adsorption method (PSA). PSA had a higher impact in all categories due to high energy consumption and methane losses

Figure 6.6 shows the carbon balance of the combined removal process. Upgrading to biomethane by combined removal process emitted a total amount of 0.0397 kg of CO<sub>2</sub>



The Economic analysis is performed for all 3 scenarios. This included the technical parameters for a better understanding of the processes. The calculations included the capital investment (CAPEX) as well as the operational and maintenance cost (OPEX) for all three scenarios. It is seen that CHP plant 0.59 M€<sub>2017</sub> while PSA – AD and CRP BA – AD cost about 1.6 M€<sub>2017</sub>. According to Ullah Khan *et al.* (2017), CAPEX has been inversely related to plant size thus larger the plant size lesser is the CAPEX compared to smaller plants with high capital and operational expenditure. This is similar to all biogas upgrading and biogas utilization pathways. It is seen that capital investment of PSA AD is higher 1.4 M€<sub>2017</sub> than CRP BA - an AD which is 1.2 M€<sub>2017</sub> whereas the operational cost for CRP BA – the AD is higher 0.4 M€<sub>2017</sub>. The operation cost for PSA – the AD is 0.2 M€<sub>2017</sub>. The cost of operation of an upgrading process mainly depends on the electricity consumption, labor, water etc. However, the total plant cost is similar and does not have much difference.

The electricity consumption for PSA - the AD is evidently higher than CRP BA - AD as well as the annual and maintenance cost. Labor cost for CRP BA - AD process is higher. This may be attributed to the bottom ash loading and unloading process which could be a tedious operation. In case of PSA process, the adsorption occurs where CO<sub>2</sub> is fixed under high pressure. When pressure is released, desorption occurs and hence the sorbent is regenerated. The total biogas produced by scenario 1 amounts to 192,000,00 kW/year.

The combined heat and power generation (CHP) plant of scenario 1 has an electrical efficiency of 35 % and a thermal efficiency of 50 % with losses up to 15 %. The energy efficiency of CHP unit is less compared to biogas upgrading pathway because biogas upgrading produces biomethane by the removal of unwanted gases thus increasing the end calorific value and the energy content of biomethane. Wu *et al.*, (2016) calculated the energy efficiency of CHP system and biogas upgrading unit and found out that the overall plant energy efficiency was 46.5 % for biogas upgrading and only 30.4 %. In CHP, raw biogas is converted into heat and electricity thus the latter two being as secondary output energy carriers decreasing the overall efficiency. Albeit the heat from CHP can be utilized 100 %, the overall efficiency is still less due to the losses in CHP. With no incentive for heat in Germany, the amount of electricity produced per annum equals to 672,0000 kW/year. According to EEG act, the revenue for renewable electricity is 0.08 €<sub>2017</sub>/kWh<sub>el</sub>. Hence total income using CHP plant thus will amount to 537,600 €/year.

Scenario 2 consists of Pressure Swing Adsorption process with aerobic desulphurization termed as PSA - AD. The plant upgrades raw biogas of 400 m<sup>3</sup>/h to biomethane at 260 m<sup>3</sup>/h with an increased calorific value of 10.56 kWh (Wu *et al.*, 2016). The methane content is usually >97 %. Thus the total annual energy production

of upgraded biomethane is 219,648,00 kW/year. Scenario 3 consists of combined removal process consisting bottom ash CO<sub>2</sub> capture and aerobic desulphurization (CRP BA – AD) that upgrade raw biogas to biomethane similar to scenario 2. It is essential to analyze the income for biomethane due to various incentivization schemes. According to the statistical portal publishing, the volume of biomethane injection into German gas grid was 106,800 m<sup>3</sup>/h. Though there is no immediate compensation for biomethane feed-ins, the German energy industry act (EnWG) facilitates biomethane access to the national gas network with agreements between gas supplier and transmission operator. Thus, GasNZV regulates the costs of connection of biomethane to the gas network will be divided with biomethane supplier (25 %) and the grid operator (75 %). Also, the avoided network fee 0.7 € cent / kWh is given as a bonus for biomethane supply to gas grids. The electricity production from biomethane CHP plants for biowaste plants has an incentive of 0.013 € /kWh (Bundesregierung, 2014)

Hence the total energy produced from biomethane CHP from both plants scenario 2 and scenario three will amount to 21,964,800 kW/year. The corresponding revenue for electricity from biomethane amounts to 285,542.4 €/year. Apart from income and subsidy in biomethane plant, the CRP BA - AD plant from scenario 3 has an additional income for the gate fee entering gate fee amounting to 28 € / ton for incoming bottom ash in Germany hence a total income of 1,120,000 € / year. Thus, it is undisputed that scenario with biomethane plants are profitable than CHP plant. This is associated with the higher incentives for electricity from biomethane gas feed into the gas grid. If there is no revenue for electricity from biomethane powered CHP, CRP BA - AD still shows an income from entering bottom ash as gate fee.

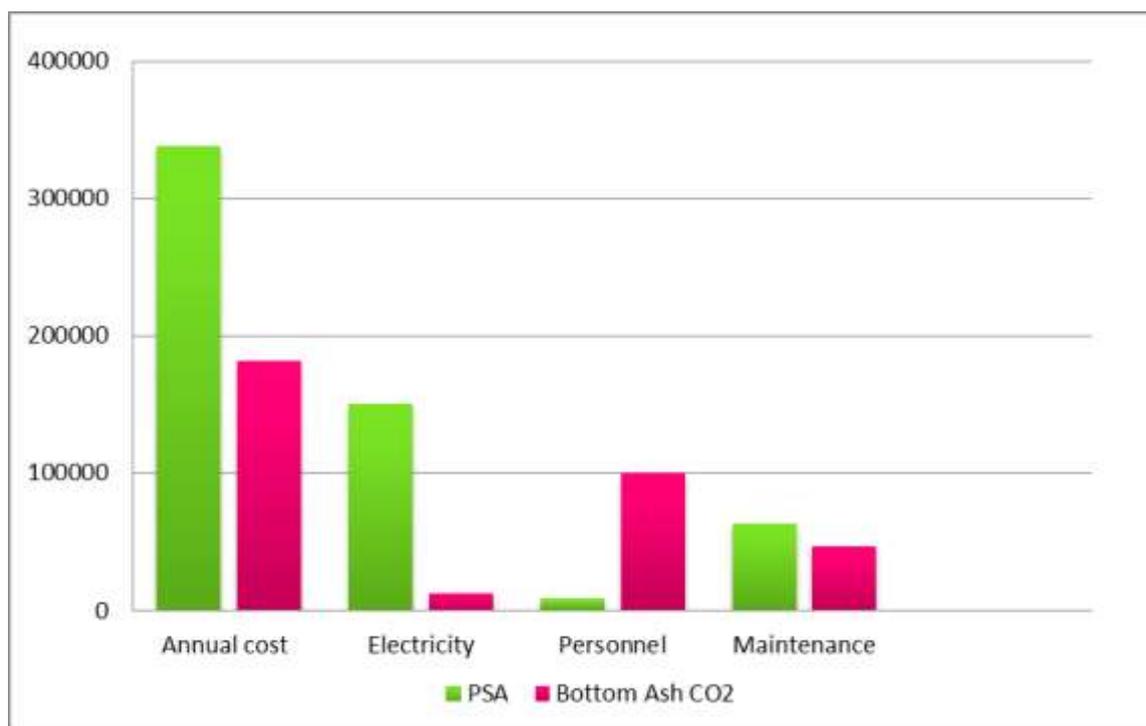


Figure 6.7: Comparison of operational expenditure (OPEX) for Pressure swing adsorption (PSA) and combined removal process.

However, this is closely related to the distance of the bottom ash collection and upgrading plant. Pertl, Mostbauer, and Obersteiner, (2010) found that increasing distance from the bottom ash collection point and upgrading plant increases both costs as well as the environmental greenhouse gas emissions. The economic analysis shows that role of incentives plays a significant role in implementing biomethane CHP as compared to burning raw biogas in CHP.

The reason is due to the current market price for electricity and biomethane due to the amendment of (EEG, 2017) in Germany. The profitability of an upgrading technology is dependent on the cost of biomethane as compared to the cost of natural gas. The price of biomethane is usually 2 - 3 times higher than the cost of natural gas hence it is significant to choose an upgrading technology with higher economic benefits (Horschig *et al.*, 2016).

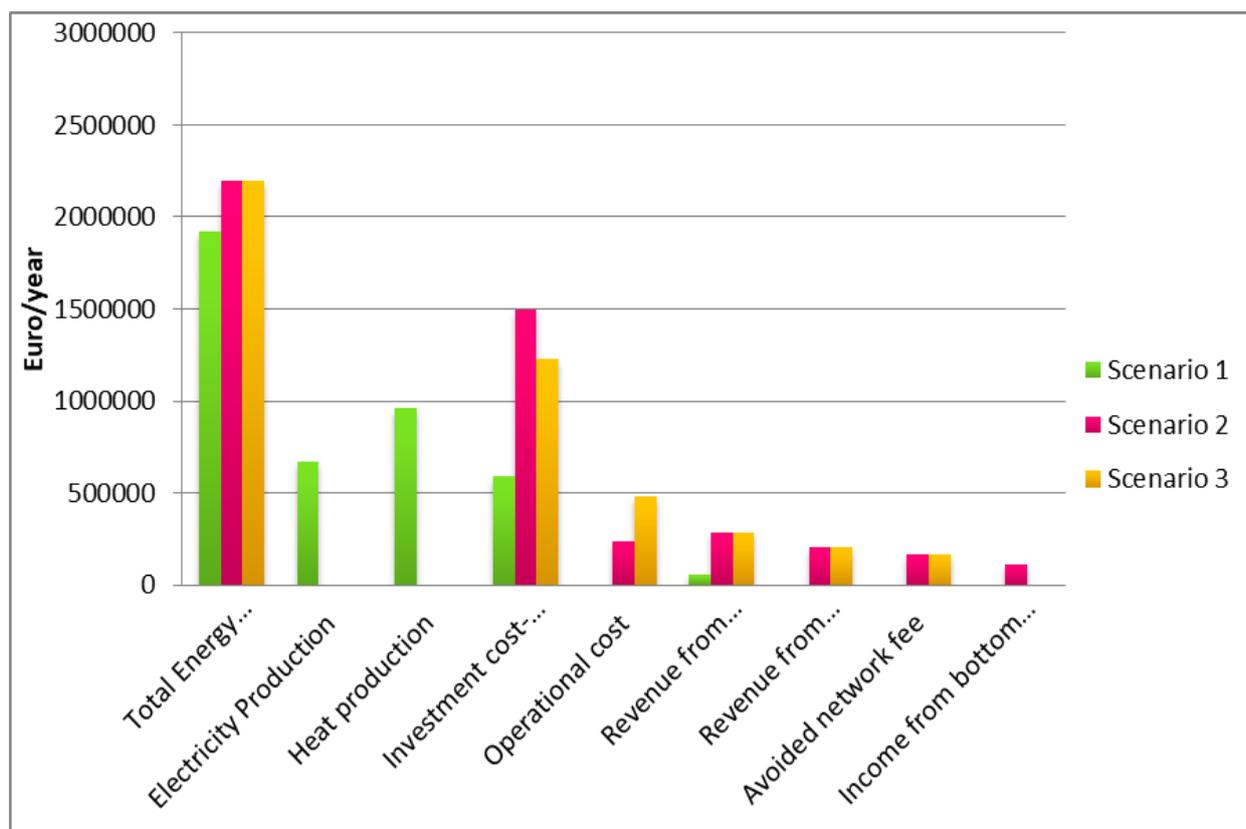


Figure 6.8: Economic comparison of three scenarios; Biogas with CHP, Pressure swing adsorption with aerobic desulphurization (PSA - AD) and Combined removal process with aerobic desulphurization (CRP - AD)

With the amendments made by EEG in 2017, the biomethane plants will have to face significant challenges and requirements. The introduction of auction system by EEG 2017, limits the participation of biogas plants in contributing to the renewable energy sector. Especially choosing lower capital cost technologies such as aerobic desulphurization and low carbon technologies such as bottom ash would be more reasonable than investing in higher costing upgrading technology. Due to the participation of tenders with plants >150 KW in auction and bidding system, more plants with less installed capacity may arise (Thrän *et al.* 2014).

This, in turn, is favorable for bottom ash technology as the availability of bottom ash to be used for CO<sub>2</sub> capture will be abundant.

Table 6-3: Techno-economic analysis data for three Scenarios

	Units	Digestion with Cogeneration unit (CHP)	Scenario 2 Aerobic desulphurization with PSA (PSA - AD)	Scenario 3 Aerobic desulphurization with bottom ash adsorption (Combined removal process) (CRP BA - AD)
Raw biogas inflow	m <sup>3</sup> /h	400	400	400
Electric energy required	KW		132	65
Biogas after upgrading	m <sup>3</sup> /h	-	260	260
Operational hours	h/year	8,760	8760	8760
Gas quality	-	Low	Medium	High
Methane loss	%	-	0.78	<3
Methane efficiency		Low	High	Medium
Methane content	%	91-100	>96	91 -100
Operating pressure	bar	-	-	4 - 7
Total energy production <sup>g</sup>	KW/year	19,200,000	21,964,800	21,964,800
Electricity production <sup>a</sup>	KWh/year	6,720,000	-	-
Heat production <sup>b</sup>	KWh/year	9,600,000	-	-
Investment costs (CAPEX)	Euros Million	0.59	1.2	1.4
Operational cost (OPEX)	Euros/year	-	482,140	234,539
Revenue from electricity <sup>c</sup>	Euros/year	-537,600	-285,524.4	-285,524.4
Revenue from biomethane sale <sup>d</sup>	Euros /year	-	-	-
Avoided network fee (bonus) <sup>e</sup>	Euros/year	-	-1,683,601	-1,683,601
Income from entering bottom ash <sup>f</sup>	Euros/year		-	-1,120,000

a) assumed 35% efficiency in CHP of total energy produced to electricity

b) Assumed 50% efficiency in CHP of total energy for heat production. CHP has the electrical efficiency of 30%

c) 0.08 euro/kWh revenue for electricity produced

d)0.92 eurocents/kWh for biomethane sold in Germany

- e) Avoided network fee of 0.78 eurocents/kWh is given as bonus
- f) Income from bottom ash 28 euro/ton. Source from AVEA GmbH, Germany
- g) The upgraded biogas called biomethane will have high energy content (56 MJ or 12 kWh)

Given EEG amendment 2017, and replacement of biofuel quota with greenhouse emission reduction quota, the biogas plants and the biofuel market in Germany has an extra burden to prove higher GHG savings and to choose a successful technology in the new framework.

The increased GHG reduction has to be met by petrol companies with a penalty of 470Euro/ ton of CO<sub>2</sub>. Thus petrol companies have to look for biofuels with best CO<sub>2</sub> savings as well as the cost ratio. Notably, the EU Emission Trading Scheme (European Commission, 2016) has started to invest in decarbonizing and low carbon technologies. Various EU initiatives such as Strategic Energy Technology Plan (SET-Plan) (Commission, 2012) and NER 300 have funded CCS technology with an aim to meet its 2030 greenhouse gas emission target.

Thus Carbon capture and storage technology (CCS) such as bottom ash adsorption could serve this purpose. Any attempt to address the issue of CO<sub>2</sub> emission target as well as meeting the energy demand would fail with implement of technology or subsidy alone.

The current scenario is thus a contribution of both EU policy to support low carbon upgrading technology in combination with cost-effective methods.

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## 7 Conclusion and Outlook

### 7.1 Conclusion

Results from this study prove that combined H<sub>2</sub>S and CO<sub>2</sub> removal for biogas upgrading is achievable both technically and economically. However, there are specific scenarios and conditions which will favor this technology. The process which combines both aerobic desulphurizations for H<sub>2</sub>S removal and bottom ash for CO<sub>2</sub> capture reduces the net CO<sub>2</sub> emissions released into the atmosphere as compared to other upgrading technologies available in the market today.

In the present study, the performance of combined removal process was proved with lab scale as well as a pilot test study. In lab scale analysis, aerobic desulphurization was studied by passing H<sub>2</sub>S gas at various concentrations. Molecular FISH analysis aided in identifying the Sulfur-oxidizing bacterial population that carried out the H<sub>2</sub>S degradation process. Furthermore, CO<sub>2</sub> removal was accomplished by carbonation reaction with bottom ash. Weathered bottom ash from Municipal incineration plant in Leverkusen, Germany was used for the entire study. Experiments from the lab-scale study revealed that bottom ash was able to capture and store CO<sub>2</sub> gas in the form of mineral carbonate. Since lab scale process was tested with only a mixture of biogas stimulus (gas mixture of H<sub>2</sub>S and CO<sub>2</sub>), the testing of the experimental rig at the biogas facility in Metabolon landfill site, Cologne proved the feasibility of this technology in a real time application.

The study shows that implementing biogas upgrading using combined removal process is feasible environmentally which was proved using life cycle analysis. Some of the essential findings and conclusions of the study are summarized as follows.

Biological H<sub>2</sub>S removal was accomplished by inoculating oxidizing sulfur bacteria in bio trickling filter column. After the startup phase of passing H<sub>2</sub>S gas into the column, the following results were identified.

- The ability to degrade H<sub>2</sub>S content in biogas with 99 % removal efficiency with the loading rate of 14.2 g S- H<sub>2</sub>S m<sup>-3</sup>.h<sup>-1</sup>
- It is found that when Empty bed resident time (EBRT) was decreased from 250s to 43s, the removal efficiency of the biotrickling filter also decreased thereby denoting a critical residence time for biotrickling filter operation
- The production of sulfate content in recirculation liquid in biotrickling filter increased with increasing loading rate. Thus, when the loading rate was 14.2 g S- H<sub>2</sub>S m<sup>-3</sup>.h<sup>-1</sup> the sulfate produced was only 0.7 [S-SO<sub>4</sub><sup>2-</sup>] produced (g/L), whereas when the loading rate was increased to 85.7 g S- H<sub>2</sub>S m<sup>-3</sup>.h<sup>-1</sup>, the

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sulfate produced was 34.1 [S-SO<sub>4</sub><sup>2-</sup>] produced (g/L). This proves that the biological oxidation has taken place with the help of sulfur-oxidizing bacteria.

- Molecular FISH analysis revealed a diverse population of sulfur-oxidizing bacteria in the biological aerobic desulphurization set up. Fluorescently labeled probes THIO1 and ALF 968 targeting the *Acidithiobacillus spp* genus and the related alphaproteobacterial species produced signals when extremely acidic sulfur-rich inoculum from bio trickling filter was used for identification.
- Bottom ash used for CO<sub>2</sub> absorption showed a more significant breakthrough time with low flow rates of CO<sub>2</sub> gas. This was proven when bottom ash of 400 mg showed breakthrough time of 40 mins when the flow rate of CO<sub>2</sub> gas from the gas cylinder was adjusted to as low as 10 ml/min. Lower flow rates gave better gas contact time with bottom ash
- Moisture content played a significant role in the bottom ash carbonation reaction. Liquid /solid ratio (L/S) with 0.1 showed longer breakthrough time than L/S between 0.05 and 0.2. Thus, optimum moisture content in bottom ash is a prerequisite for CO<sub>2</sub> capture
- The sorption capacity of bottom ash with ratio L/S = 0.1 also showed greater CO<sub>2</sub> uptake. It was evident that bottom ash with finest 0 -2 mm fractions containing L/S ratio = 0.1 showed high sorption capacity of 14.56 g CO<sub>2</sub>.kg<sup>-1</sup>
- The integrated process for H<sub>2</sub>S and CO<sub>2</sub> removal termed as combined removal process was tested for its performance at biogas plant facility situated in Metabolon Landfill site, Cologne. Results showed that it was technically feasible to operate the combined removal process with real biogas.
- The combined removal process was mutually beneficial as bottom ash was able to absorb H<sub>2</sub>S from biogas thereby complementing the biological aerobic desulphurization process.
- During combined removal process operation, inorganic carbonate supply was in the form of gaseous CO<sub>2</sub> from biogas. The FISH analysis was performed to see variations in the bacterial population. Albeit, the autotrophic sulfur-oxidizing bacteria remained as a stable population efficiently utilizing the gaseous CO<sub>2</sub>.
- Life cycle analysis (LCA) was performed to study the environmental impact as well as the global warming potential of the combined removal process. Both processes proved to emit CO<sub>2</sub> minimally. Individually, aerobic desulfurization contributed 0.012 of the total 0.037 kg of CO<sub>2</sub>- Eq emitted for the upgrading 1 KWh of biomethane
- It is noted that electricity consumption caused the significant contribution in all impact categories studied in life cycle analysis followed by transportation. Primarily, the impact caused by electricity consumption regarding global warming potential was 56.8 % whereas, in all other categories, the electricity consumption contributed more than 80 %. Methane losses do cause a significant impact on global warming potential with 38.1 % followed by transportation of 5.31 %.

- Liquid emissions from aerobic desulphurization caused a significant impact on photochemical oxidation potential. However, this could be nullified with proper wastewater treatment
- A comparison of LCA for combined removal process with market available Pressure swing adsorption method showed that the latter contributed higher environmental impact. This is due to the high energy requirement as well as the methane losses. Methane losses in PSA are usually higher than other upgrading technologies in the market. Since bottom ash can capture and store CO<sub>2</sub>, the net overall process emissions in combined removal process are negligible as compared to that of PSA.
- However, to achieve less environmental impact, it is advisable to implement the combined removal in a scenario where the Biogas plant is at the same site as that of an incineration plant. In this way, the impact due to the transportation of bottom ash could be minimal
- In such case, it is also possible to deliver high amounts to bottom ash to a landfill where small to medium amounts of "lean landfill gas" (gas high in CO<sub>2</sub>, but low in CH<sub>4</sub>) are available, to prolong conventional utilization in existing gas engines.
- A techno-economic analysis compared three scenarios with biogas CHP, biogas combined removal process and biogas pressure swing adsorption revealed that biogas combined removal process has high economic benefit due to the income of gate fee from incoming bottom ash. Though there is an income of selling the bottom ash after carbonation, it was excluded in this study due to its minimal economic benefits. If tipping fees for carbonated ash are distinctly lower. This has to be checked in any case and about national landfill regulation (classes of landfills, leaching limits for pH, Lead, Sulfate, etc.) and the actual local tipping fee levels. In this case, the economic driver is "ash treatment" and not "improvement of gas quality."
- Using CHP with biogas is less attractive due to limited efficiency of the gas engine with typical 15 % energy losses. However, with support schemes for biomethane in CHP in countries such as Germany makes CHP an economically viable option to produce renewable electricity.

## 7.2 Outlook

Unlike other biogas upgrading methods, combined removal process for biogas upgrading proves its ability in reducing the overall greenhouse gas emissions (GHG) which is the primary driver for the EU energy policy. This process was developed by introducing a new biogas upgrading technology combining low cost, less energy requirement with minimal CO<sub>2</sub> emissions. This study indicated that combining biological aerobic desulphurization with bottom ash for CO<sub>2</sub> removal proved technically as well as environmentally feasible. Technically, albeit feasible, the final methane content after upgrading may have suffered a nitrogen inclusion. Further study with attempts made to enhance the methane content for this process is necessary. Environmentally, life cycle analysis proved the low carbon emission benefits of this process as compared to pressure swing adsorption and aerobic desulphurization. However, to operate successfully, the implementation of this process solely relies on scenarios where the availability of bottom ash is abundant, and the transportation is made more accessible. Studies that involve the use of renewable energy for the transportation could give more profound insights in this case. Biogas plant nearby a landfill site could be a suitable example. Economically, combined removal process has higher profitability due to the gate fee for bottom ash. In this case, the only factor that increases the economic profitability of this process is the tipping fee for bottom ash. Biogas upgrading, in general, poses a high capital expense (CAPEX) and operational expense (OPEX). The choice of using biogas upgrading as compared to CHP purely relies on support schemes and incentives from EU.

With the introduction of the auction in new support schemes (EEG 2018), all biogas upgrading methods will suffer a setback in Germany. However, the introduction of new schemes in carbon capture and storage technology (CCS) by EU ensured that such technologies have a more significant potential in reducing the global GHG emissions. In this study, combined removal process was proved with high GHG emissions savings. This study explored the possible options of low carbon upgrading technology in the field of biogas upgrading and bioenergy supply chain. However, for such technologies to become practical and successful, a definite help favoring low carbon emission technologies in the form of incentives and other support schemes from the government is indeed needed. Future analysis could then identify a new chapter of low carbon biogas upgrading technologies.

		<b>Operating Instruction</b> <b>nach §9 BetrSichV</b>		Number: XXX
<b>Department: Civil Engineering</b> <b>Institute: Urban Waste and Water Management</b>		<b>Responsible:</b>		
<b>Written by: Keren Jenifer Rajavelu</b>		<b>Date:</b>		
<b>1. Area of application</b>				
This instruction describes the adequate operation of a continuously run lab plant for biogas upgrading unit. The setup contains of one aerated bioreactor with a suspended growth culture dominantly containing <i>Acidithiobacillus sp</i> in combination with bottom ash reactor for CO <sub>2</sub> removal in upgrading unit.				
<b>2. Hazards for Human and Environment</b>				
          	The process utilizes Biogas from the site with following substance:			
	Description	H-/P-Statements	Range of Exposure	Hazard condition
	Methane CH <sub>4</sub>	H201,H203,H221,H250,H270,H318,H335,P202,P280,P341,P377	Explosive range 4.4% - 16.5 %	Danger of suffocation
	Carbon dioxide	H315,H336	MAC 5000ppm=0,5%; dangerous area above 8 Vol %	Danger of suffocation
	Oxygen O <sub>2</sub>	P370+P380	concentration below 18 Vol % is dangerous	Danger of explosion
Hydrogen Sulphide H <sub>2</sub> S	H201,H203,H221,H250,H270,H318,H335,P282,P311,P313,P341,P370+P376,P373	MAC 10 ppm = 0,001 % 50 ppm 0,005 % = irritation of the respiratory tract 200 ppm 0,02 % = paralyzed sense of smell 700 ppm 0,07 % = respiratory arrest (death)	colourless, smelling like rotten eggs heavier than air, strong blood and nerve poison	
Ammonia NH <sub>3</sub>	EUH070,EUH071,H410,H372,H221	danger of fire 15 % - 30 % MAC 20 ppm = 0,002 % 30 - 40 ppm = irritation of mucousmembranes, respiratory tract and eyes 1000 ppm = 0,1 % = difficulty in breathing, unconsciousness.	colourless, pungent smelling and lighter than air Extremely corrosive upon skin exposure, able to corrode metals	
The process utilizes following biological materials:				
Used substance	Description			
<b>Suspended growth culture</b>	The reactor contains a suspended growth culture which is dominated by the organisms <i>Acidithiobacillus sp</i> . Due to the environmentally close cultivation conditions, a cross-contamination with other microbes in the system can not be ruled out. The previously mentioned microbes are not considered as pathogenic to humans.			
The Process utilizes following chemical substance:				
Chemical compound	Physical/Chemical characteristics	Fire and Explosion Hazard data	Health hazard condition	
Bottom ash	Boiling Point : > 1400° C pH : N/A Solubility in Water: N/A Specific Gravity: 2.3 to 2.7 Appearance and odor: Grayish granular material; indistinctive odor.	Flash point: N/A Flammable Limits : N/A Extinguishing media : N/A Unusual and explosive Hazard: N/A	Effects of Overexposure: Acute - Irritation of eyes, skin and mucous membranes. Chronic - Fibrotic diseases of the lungs and potential carcinogenicity.	

3. Safety- and behavioural measures	
  	<ul style="list-style-type: none"> <li>• The windows must be open</li> <li>• Always ventilate rooms so that there is no lack of oxygen or a dangerous gas concentration can arise.</li> <li>• Avoid ignition sources (e.g. smoking, no work with spark producing tools, measures against electrostatic charges taken for potential balancing).</li> <li>• Do not smoke, eat or drink. Avoid inhalation of vapors. Avoid contact with the skin.</li> <li>• Wearing safety glasses (DIN EN 166) during the whole time is mandatory. Wearing nitrile gloves during the whole time is mandatory. Gloves have to be exchanged regularly.</li> <li>• In between the exchange, hands need to be washed and disinfected.</li> <li>• Wearing a lab coat during the whole time is mandatory.</li> <li>• Avoid contamination!</li> <li>• Eating, drinking or storing food or beverages in the laboratory and/or while wearing safety gear is forbidden.</li> <li>• Disinfect workspace after finishing your work.</li> <li>• Dispose contaminated material in appropriate containers.</li> </ul>
4. Behaviour during plant failure	
	<p><u>During leakage or exhaustion of material:</u></p> <ul style="list-style-type: none"> <li>• Quit danger area room, superiors informed.</li> <li>• If possible without risks, shut off gas supply or leakage.</li> <li>• In the case of damage removal, if adequate ventilation is not possible, wear protective respiratory device.</li> <li>• In the early stages of a fire: Use chemical fire extinguishers.</li> </ul> <p><b>Caution! The pH-value of the utilized chemicals is adjusted between 1 and 3. !</b></p> <p>Inform concerned person immediately!</p>
5. First Aid <span style="float: right;">Emergency call: 112</span>	
	<p><b>Emergency and First Aid Procedures:</b></p> <p><b>Inhalation:</b> Move to ventilated area.</p> <p><b>Skin:</b> Wash with mild soap and water.</p> <p><b>Eyes:</b> Flush with flowing water for 15 minutes.</p> <p><b>Consult medical attendance</b></p> <p><b>Life-saving emergency measures must be carried out depending on the situation.</b></p>
6. Maintenance, Disposal	
	<ul style="list-style-type: none"> <li>• Maintenance only by qualified personnel</li> <li>• After completion of work, dispose materials in appropriate containers</li> <li>• Responsible for maintenance: Keren Jenifer Rajavelu, Prof. Denecke</li> </ul>

Date:..... Signature:.....

(Verantwortlicher/Leiter des Arbeitskreises)

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