PhD THESIS PROPOSAL

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PROGRAMME: **Environmental Engineering**
TITLE OF THESIS: **DESULFURIZATION OF BIOGAS USING A MEMBRANE BIO-SCRUBBER**

INTRODUCTION:

Biogas is a renewable and sustainable energy source which is produced by anaerobic fermentation of organic matter. The nature of the raw materials and the operational conditions used during anaerobic digestion processes will determine the chemical composition of the biogas. The raw biogas consists mainly, 40-75% of CH_4 and 15-60% CO_2 and minor constituents such as H_2S (Hagen et al., 2001, Krich et al., 2005). Due to its calorific value, biogas is a potential energy source and it can be used for many applications such as gas fuel for vehicles and heat and power generation, feedstock for chemical production, and natural gas replacement (Lau et al., 2011; Tippayawong, 2011).

H_2S transfers into the gas phase as a minor component of the biogas and restricts the direct use of raw biogas as a fuel. In addition to its unpleasant odor, H_2S gas is highly toxic (Syed, et al., 2006; Tang et al. 2009), accelerates the corrosion of utilities (combustors, compressors, engines, boilers, etc.) and reduces lifespan of pipe work and other installations. The concentration of H_2S in biogas can range from 0.1 to 2% v/v (1000-20,000 ppmv) (Fortuny et al., 2011), whereas manufacturers of combined heat and power (CHP) production units recommend limiting values between 0.01 and 0.03% v/v (100-300 ppmv) to control corrosion problem in piping systems and equipment, rarely unexpected peaks are allowed (Ramous et al., 2014). Therefore, H_2S concentration in the biogas has to be controlled in order to prevent the damage and fulfill the quality standards required according to the final usage of the biogas (Deublein et al., 2008).

There are several technologies available for biogas desulfurization; based on physical (Belmabkhout et al., 2009), chemical (Peiffer and Gade, 2007) or biological principles (Chung et al., 2007; Lin et al., 2013). Although the physical desulfurization technologies such as membrane separation, water scrubbing and activated carbon adsorption are quite effective, they are not economical because of periodical replacement/regeneration costs of the consumed media (Ryckebosch et al., 2011). Chemical processes have also high operating costs because of the consumption of significant amounts of chemicals such as caustic soda

and iron salts (Table 1). Besides they produce secondary chemical wastes that should be treated properly before disposal (Lin et al., 2013). Bio-desulfurization processes are more attractive than physical and chemical processes because they can be operated inexpensively and its eco-friendliness, energy-savings and low-operating costs (Sakuma et al., 2006; Dennis and John, 2000).

The most commonly used biological processes for H_2S removal can be classified into two groups: Internal and external bio-desulfurization (Beil et al, 2010). External biodesulfurization processes may be further classified as single stage and two-stage combined systems.

Internal bio-desulfurization, which is accomplished inside the digester or the headspace, is the simplest and cheapest method that is commonly used in farm-type digesters (Beil et al., 2010). In this process, small amount of air is injected into the head space of the anaerobic reactor so that the sulfide-oxidizing bacteria (SOB) can use it to oxidize H_2S (Botheju and Bakke, 2011). Because of its low cost and availability, air is commonly used as source of oxygen. Several studies have confirmed the effectiveness of microaeration in biogas desulfurization, a disadvantage of this process is that, it can result in the accidental formation of explosion risk due to oxygen-biogas mixtures. Moreover, it results in the dilution of biogas with nitrogen gas, which decreases the calorific value of the biogas. Biogas desulfurization efficiencies above 97% can be achieved by injecting air without any impact on the digestion performance (Díaz et al., 2010a). In contrast, Jenicek et al. (2010) stated that introduction of air for internal biodesulfurization may cause aerobic decomposition of substrates and as a result the methane production could decline.

In external single-stage bio-desulfurization processes, the H_2S oxidation takes place outside the anaerobic digester. The raw biogas passes through a fixed bed reactor, filled with moist packing materials on which the sulfide oxidizing bacteria grow. As fixed bed reactor, typically biofilters (BF) and trickling filters (BTFs) are used (Burgess et al., 2001).

In both systems, the desulfurization takes place in one step in a single reactor. In this way, the investment cost reduces significantly. Difficulties in controlling the operational parameters and clogging of the packing material are the drawbacks of single-stage biodesulfurization process (Montebello et al., 2012; Rodríguez et al., 2014). However, the main problem is the dilution of the biogas with the inert N_2 gas and excess O_2 supplied to the system in the form of air. Therefore this process is not suitable if the biogas is to be used as vehicle fuel or for grid injection due to the remaining traces of especially O_2 (Petersson and Wellinger, 2009). BTFs are more widely used in odor control (Kim et al., 2005).

Two stage bio-desulfurization systems are often called bio-scrubbers. In bio-scrubbers, the gas absorption and cleaning occur separately in a two-stage process: chemical H_2S absorption with an alkaline solution followed by bio-oxidation in an aerobic bio-reactor (Gabriel et al., 2013). The major benefit of bio-scrubbers is their

ability to deal with high H_2S concentrations and also severe fluctuation. By using these systems removal efficiencies as high as 99% can be achieved (Fernandez et al., 2013). When compared with the single stage biotrickling filters, in two stage bio-scrubbers air is injected to the second bio-reactor, not to the first scrubbing unit, therefore there is no risk of N_2 and O_2 accumulation in the biogas (Allegue and Hinge, 2014). On the contrary, these systems are complex and have high capital and operational costs; hence their application range is restricted to large-scale biogas plants (Papadias et al., 2012).

Table 1. Advantages and disadvantages techniques for removal of H_2S (Syed, et al., 2006; Ryckebosch et al., 2011; Iovane et al., 2014)

Technology		**Advantages**	**Disadvantages**
Physical	Adsorption on activated carbon	High removal efficiency Low operation temperature High loading capacity	Expensive investment and operation CH_4 losses H_2O and O_2 needed to remove H_2S
	Membrane separation	Removal of >98%, CO_2 is also removed Light in weight	Expensive operation and maintenance (fouling problem) Complex
	Water scrubbing	Cheap when water is available(not regenerative) CO_2 is also removed No special chemicals requirement	Difficult technique Clogging of the absorption column possible High consumption of water (if there is no regeneration) CH4 losses
Chemical	Caustic soda	Low electricity requirement Smaller volume, less pumping, (compared to absorption in H_2O) Low CH_4 losses	Expensive investment & operation More difficult technique Not regenerative
	Iron salts	Cheap investment Low electricity and heat requirements Simple operation and maintenance No air in biogas	Low efficiency Expensive operation (iron salt) Changes in pH/temp not beneficial for the digestion process Correct dosing is difficult
Biological	Internal desulfurization	Cheap investment Low electricity and heat requirements, No extra chemicals or equipment required Simple operation and maintenance	Concentration H_2S still high Excess O_2/N_2 in biogas implies difficult upgrading or additional cleaning Overdosing air results in explosive mixture
	External single stage	Simple, flexible design Low capital Low operation and maintenance costs,	Difficulties in controlling the operational parameters clogging dilution with the inert N_2 gas and excess O_2 Explosive risk
	External two stage	More than 99% removal efficiency No risk of N_2 and O_2 mixing with biogas	Complex High capital and operational costs

AIM and SIGNIFICANCE:

In the literature, there are numbers of studies about removal of H_2S from biogas. In these studies, internal H_2S removal with microaeration of the digester's headspace; biodesulfurization of biogas externally in a single-stage biotrickling filter or in a two stage system consisting of a scrubber and a bioreactor; optimization of the biodesulfurization parameters such as pH, type of packing material, empty bed residence time and etc. were investigated intensively.

However, the removal of H_2S from biogas using a membrane biofilm process has not received much attention. Such a combined selective membrane separation and bio-oxidation process is critically important for a better quality of biogas with minimal explosion risk and dilution problem, because in this single-stage system the biogas will not directly contact with air (Table 1).

The purpose of the proposed thesis is to investigate the feasibility of external biodesulfurization of biogas in a single stage membrane biofilm reactor (MBfR) which is called membrane bio-scrubber (MBS) by testing different types of membranes and electron acceptors for sulfide oxidation. In the MBS, the biogas stream will be separated from the biofilm of sulfide oxidizers by a membrane which is selectively permeable to H_2S. One side of the membrane will be in contact with a slightly alkaline medium supplemented with nutrients and an electron acceptor such as oxygen or nitrate while the other side will be in contact with the biogas. The H_2S in the biogas side will migrate through the selectively permeable membrane and then be oxidized to elemental sulfur on the other side of the membrane by sulfide oxidizing bacteria. The small amount of CO_2 that passes through the membrane will supply an inorganic carbon source to stimulate the growth of autotrophic sulfide oxidizers.

MATERIALS AND METHODOLOGY:

Materials:

Equipment and Device:

In the proposed PhD thesis study the following equipment and devices will be used

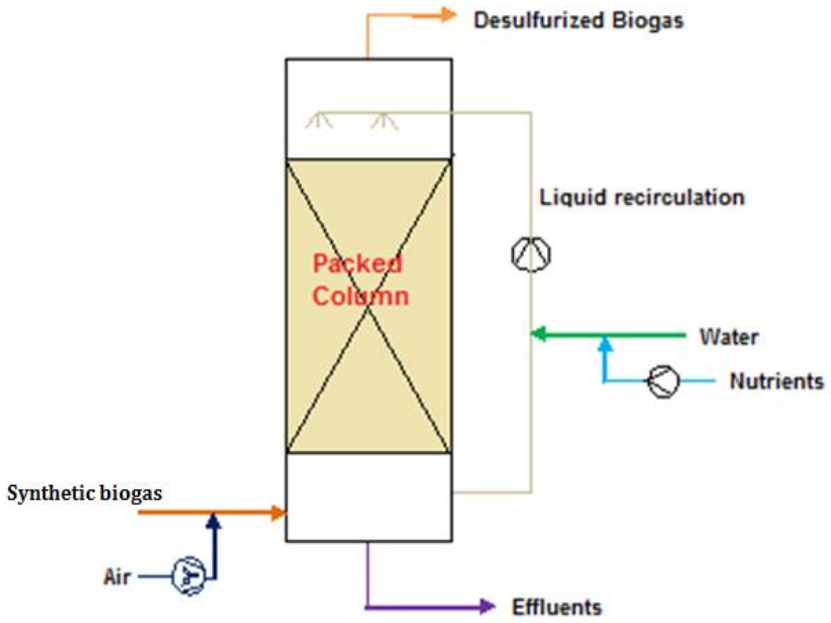
1. Shimadzu Prominence LC-20A High Performance Liquid Chromatography (HPLC)
2. Shimadzu GC-2014ATF Gas Chromatography equipped with FID and TCD detectors
3. Eutech, CyberScan PCD 6500 pH/Conductivity Meter
4. Hach-Lange HQ40D Dissolved Oxygen Meter
5. Magnetic Stirrers (Velp, SBS)
6. Milli Gascounter, Ritter Biogas-meter
7. WTW TS606 G/2i Thermostat Cabinet

8. Shimadzu 2450UV/Vis spectrophotometer
9. 323Du Watson Marlow Peristaltic pump
10. WTW Photolab 6100 Vis spectrophotometer

Methodology:

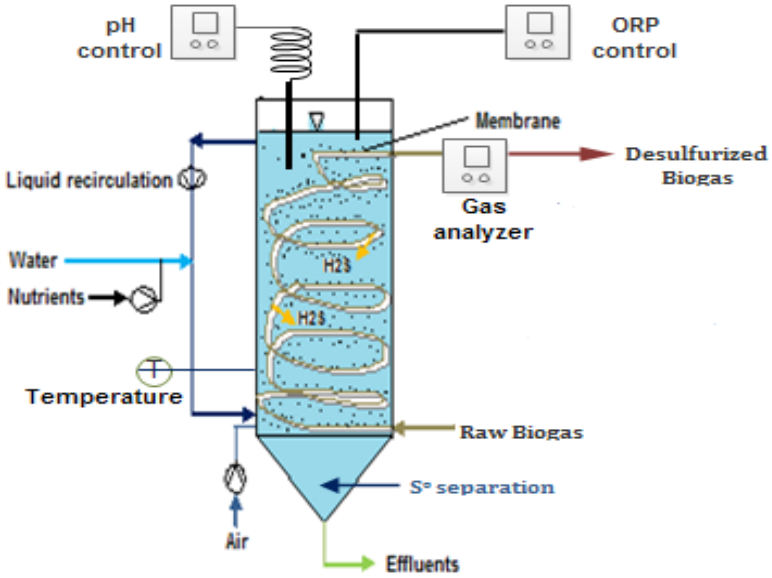
Experimental Design

1. *Desulfurization of a synthetically prepared biogas using bio-trickling filter (BTF)*



In the 1st part of the thesis study, a bio-trickling filter (BTF) will be used and its H_2S removal performance will be compared with the performance of the membrane bio-scrubber that will be tested in the next work package. In the bio-trickling filter, the H_2S will be transferred from the synthetically prepared biogas with the composition of CH_4 (60%), CO_2 (40%) and H_2S (0.15 - 0.3) to the biofilm of sulfide oxidizers that grows on the packing material made of plastic rings. The essential nutrients will be supplied to the biolfilm by recirculating a liquid phase through the packing materials in countercurrent flow. The volume of the proposed bioreactor will be about 1L in which 50% of it is packing materials. It will be operated under mesophilic conditions and a neutral pH. To remove H_2S in the liquid media *Thiobacillus thioparus* bacteria will add in a BTF reactor. Empty Bed Contact Time (EBCT), Removal efficiency (RE), Elimination capacity (EC), mass and volumetric loading rate with different influent loading rates will be tested to evaluate the systems performances.

2. *Desulfurization of a synthetically prepared biogas using membrane bio-scrubber (MBS)*
    a. Tests with (PDMS) membranes
    b. Tests with different electron acceptors (air, nitrate, ferric iron)



In the 2nd part, a membrane bio-scrubber (MBS) will be tested using selected membranes and electron acceptors for sulfide oxidation. In MBS, the H_2S in the biogas will diffuse to the liquid phase, through dense polymeric membrane, silicone (polydimethyl siloxane, or PDMS) which is selectively permeable to H_2S (Montoya, 2010). As the H_2S migrates through the selectively permeable membrane, it will enter to the nutrient rich liquid phase and be consequently oxidized by the sulfide oxidizers attached onto the surface of the membrane. The liquid phase will be maintained in a reservoir where the nutrients are refreshed, oxygen is supplied, and pH and temperature are controlled.

3. Desulfurization of the biogas of a lab-scale anaerobic digester using membrane bio-scrubber (MBS)

In the 1st and 2nd parts of the study, a synthetically prepared biogas will be used in biodesulfurization experiments. In the last part, the MBS will be tested with the biogas of a lab-scale anaerobic digester or a biogas taken from a real-scale digester.

Analytical Methods

Sulfide will be measured with spectrophotometer (WTW photoLab 6100VIS) according to the method reported by Cord-Ruwisch (Cord-Ruwisch, 1985). Sulfate analysis shall be conducted in accordance with Standard Methods (American Public Health Association, 2005). pH will be measured using Eutech, PCD 6500 pH meter.

The amount of biogas produced will be measured with a volumetric gas counter (Milligascounter, BnC-Ritter). Whereas the raw biogas composition (CO_2, CH_4, H_2S, N_2, O_2 and other gases) will be determined using a GC equipped with TCD and Carboxen-1000, 60/80 mesh, 15ft. x 1/8in. stainless steel column. The temperature of the column will initially be 35 ^oC for 5min and then be raised to 225 ^oC at 20 ^oC/min. If a

portable H_2S meter is bought, it will be used to determine the low concentration of H_2S in the effluent of MBS.

Table 2. Work Schedule

Work Package Name / Description	MONTHS											
	2	4	6	8	10	12	14	16	18	20	22	24
Procurement of equipment and consumables												
Work Package I – Desulfurization of a synthetically prepared biogas using bio-trickling filter (BTF)												
Work Package II – Desulfurization of a synthetically prepared biogas using membrane bio-scrubber (MBS)												
Work Package III- Desulfurization of the biogas of a lab-scale anaerobic digester using membrane bio-scrubber (MBS)												
Preparation of progress reports and the final report (thesis)												

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