Faculty for System and Process Engineering

# Literature survey

By


Ajinkya Sunil Kunjir


# Biogas Purification

Lecture: Sustainability assessment (LCA) for Biofuels

Lecturer: Dr. Liisa Rhiko-Struckmann

Matrikel No.: 221210

Date: 26.05.2019

# TABLE OF CONTENTS

## ABSTRACT

The need to produce fuels emitting greenhouse gases that have low life-cycle is a main parameter in the reduction of environmental impacts directly connected to human activities. Biogas, a renewable source of energy and a replacement for fossil fuels is produced by anaerobic degradation of organic waste in absence of oxygen, as shown in figure 1. It contains mainly three compounds, that are methane ($CH_4$~50-70%vol), carbon dioxide ($CO_2$~20-25%vol) and nitrogen ($N_2$~0-10%vol). The upgrading of biogas is biomethane, by removing $CO_2$ and other contaminants it allows the fuel to reach the specifications suitable for the injection in the natural gas grid and the use as vehicle fuel. This pathway enables the conversion of wet biomass into a perfect substitute of natural gas. Biogas upgrading is usually performed through CO2 removal. In this literature survey, different biogas purification techniques have been studies. This survey studies the working principles of these techniques, their advantages and disadvantages, also their efficiencies are compared. The investment costs, operational costs, environmental impacts have also been studied.

# 1. INTRODUCTION

Energy is a vital part of our daily lives. As a result, the world is facing a huge energy crisis due to continuously depleting oil reserves [1]. The problems caused by availability of oil reserves and present global warming problems caused due to the emission of carbon dioxide ($CO_2$) on burning of fossil fuels tends the people to encourage the development and utilization of alternative and renewable sources of energy [2]. Energy production from renewable sources is currently a main focus of the world at large. Numerous technologies are being studies and applied to obtain energy from different sources such as solar energy, wind energy, hydropower, geothermal, biofuel and biomass [3]. The need to produce fuels emitting greenhouse gases that have low life-cycle is a main parameter in the reduction of environmental impacts directly connected to human activities [4].

Renewable biogas from anaerobic fermentation is an energy source that is receiving importance nowadays [5]. Biogas is basically a mixture of combustible gases formed through decomposition of organic gases in anaerobic (oxygen deprived) conditions. United states and European union has recognized biogas as a clean and renewable energy for transportation that can replace fossil fuels [6] [7]. Biogas not only reduces the household waste, city sludge and other wastes but it also plays a positive role in the remission of severe greenhouse gas effects [8] [9]. The primary constituent of biogas is methane ($CH_4$~65vol%) and secondary constituent is carbon dioxide ($CO_2$~35vol%). Hence, an upgradation of biogas is necessary to remove $CO_2$ and other impurities present to use it as vehicle fuel [7].

# 2. BIOGAS – STATE OF ART

Biogas, a renewable source of energy and a replacement for fossil fuels is produced by anaerobic degradation of organic waste in absence of oxygen, as shown in figure 1. It contains mainly three compounds, that are methane ($CH_4$~50-70%vol), carbon dioxide ($CO_2$~20-25%vol) and nitrogen ($N_2$~0-10%vol). Additionally some trace elements like hydrogen sulphide ($H_2S$~0-

8%vol), hydrogen ($H_2$~0-1%vol), oxygen ($O_2$~0-2%vol) are also present [2] [6]. The calorific value of biogas ranges from 22000-25000 $kJm^{-3}$. Methane being one of the main components of biogas, its calorific value is as high as 39000 $kJm^{-3}$ after $CO_2$ is removed. It is referred as biomethane. Therefore, to maximise the utilization efficiency of biogas, it is necessary to purify biogas before its use [1] [9].

The market for biogas digester systems is fast growing and expanding, characterised by a number of suppliers, each one offering their own technology for biogas upgradation [5]. According to Hialong et. al [7] $CO_2$ being the by-product of upgrading, negative $CO_2$ emission can be controlled by capturing and storing the $CO_2$ removed from the raw biogas. The global biogas industry has a promising future, that the annual global raw biogas production will exceed 56.6 billion cubic meters by 2024. There is huge potential for $CO_2$ capture due to the rapid growth of biogas industry. For example, assuming if 50% of raw gas is upgraded, it would result in a $CO_2$ capture of 19.4 Mton [7].

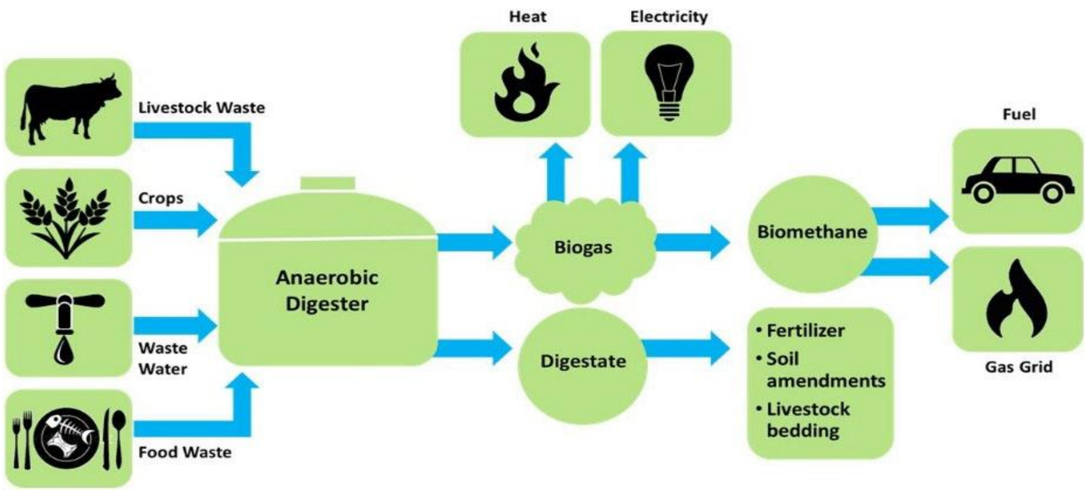


Figure 1: Anaerobic digestion process (source: google images).

# 3. BIOGAS PURIFICATION

The methods for purifying biogas mainly include absorption using water scrubbing, chemical scrubbing, membrane separation, and pressure swing adsorption (PSA) [8]. These methods can be characterised by their methane emissions, electricity use, heat use and waste produced, as presented in Table 1 [5].

Absorption with organic amine solution is efficient but the generation of amine solution involves high energy consumption and higher potential of corrosion, which are not environment friendly. For Membrane separation, membrane itself is very costly, it often suffers thermal shocks and chemical corrosion and easily gets contaminated. Adsorption does not involve equipment corrosion and environmental pollution, but its usage is limited due to high operational costs, many adsorption-desorption cycles and its complex equipments. Water scrubbing method is a physical absorption process, mainly depending on pressure and temperature. It is environment friendly process having low operational costs [8]. Figure 2 shows current technologies in biogas upgradation.

Table 1: Qualitative assessment of biogas processing techniques (data from [5]).

| Technology | $CH_4$ Emissions | Electricity use | Heat use | Consumables / wastes |
|---|---|---|---|---|
| Membrane separation | - | 0 | - | + |
| Water scrubbing | - | 0 | + | - |
| PSA | - | - | + | + |
| Chemical scrubbing | + | 0 | - | - |

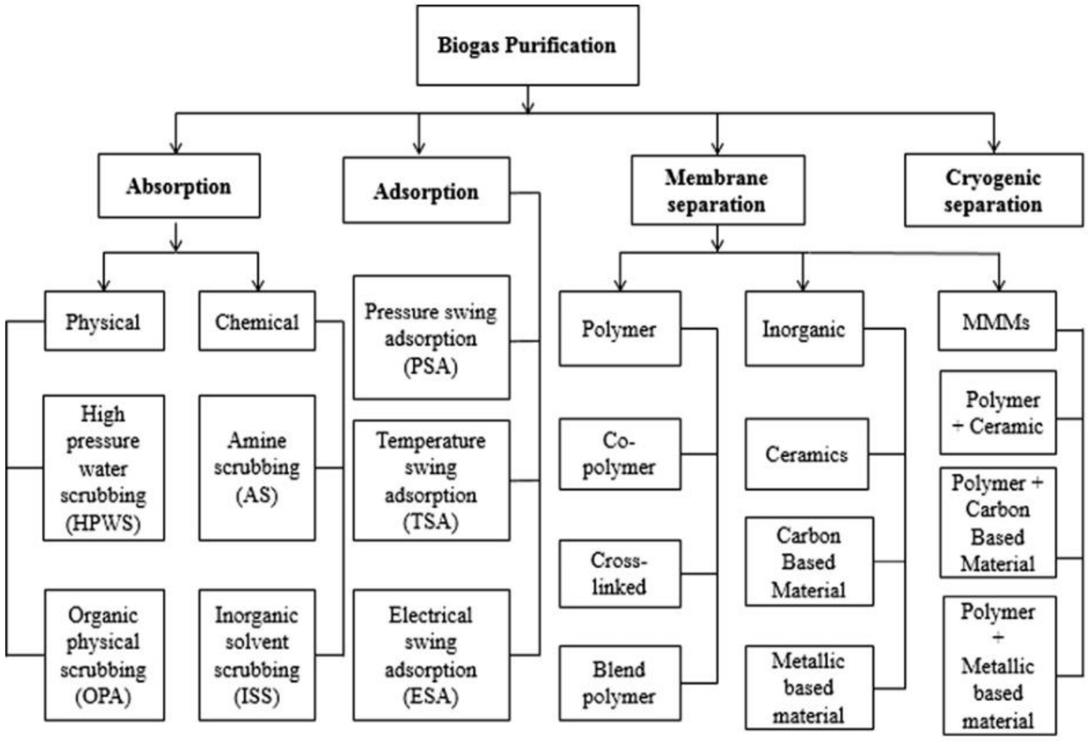


Figure 2: Current technologies in biogas upgradation [10].

### 3.1 MEMBRANE SEPARATION (MS)

In the membrane-based gas separation, the membrane acts as a permeable barrier allowing specific compounds to pass through, depending on the system pressure, temperature and difference in the concentration. For biogas upgradation, $CO_2$ permeates through the membrane and $CH_4$ is retained on inlet side as retentate (shown in Figure 3). This process is more beneficial if the gas flow is low and inlet $CO_2$ content is high. These considerations are suitable for a biogas upgrading plants [10]. Figure 4 shows process flow diagram of membrane separation.

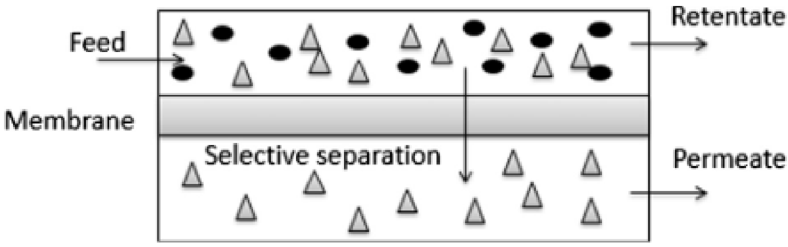


Figure 3: Scheme of membrane gas separation process [10].

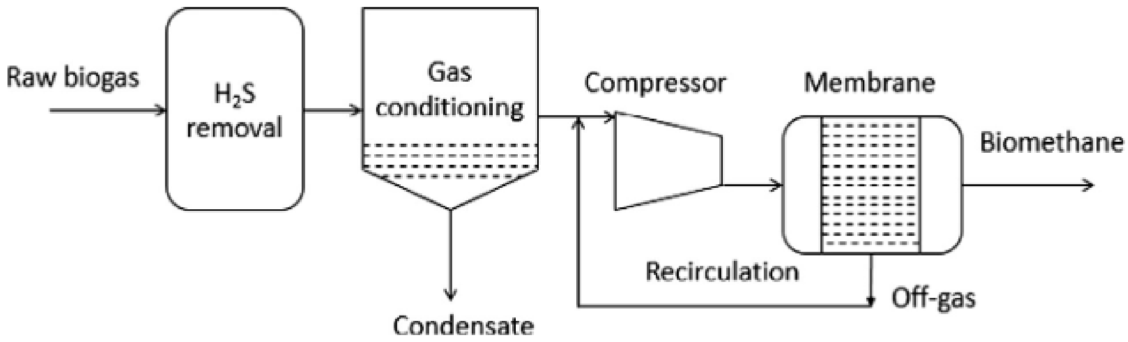


Figure 4: Process flow diagram of membrane separation [10].

## 3.2 HIGH PRESSURE WATER SCRUBBING (HPWS)

High pressure water scrubbing is the most commonly and widely used process for removal of $CO_2$ and $H_2S$ from raw biogas, as these gases are more soluble in $H_2O$ than in $CH_4$ [10]. It is a physical absorption process, in which the change of $CO_2$ solubility in water depends upon pressure and temperature. Hence, the absorption and desorption of $CO_2$ and $H_2S$ can be achieved in water. Henry's law governs the physical absorption of gases, i.e. at constant temperature the amount of any dissolved gas is directly proportional to its partial pressure. Lower temperatures results in higher solubility of $CO_2$ [8] [10]. Figure 5 shows the process flow diagram of high-pressure water scrubbing.

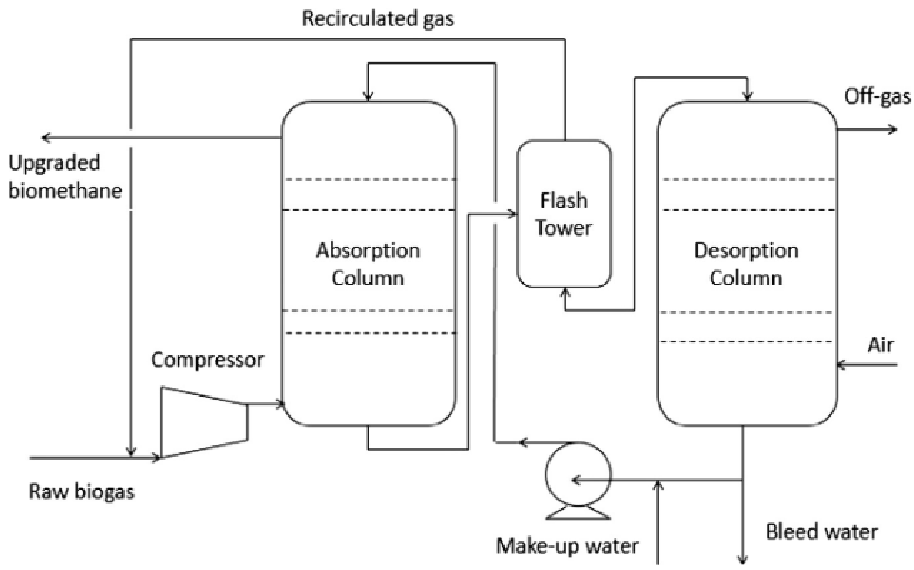


Figure 5: Process flow diagram of high pressure water scrubbing [10].

### 3.3 PRESSURE SWING ADSORPTION (PSA)

In adsorption process, solute in the gas stream is transferred on to the surface of adsorbent due to physical or van der waals forces. In pressure swing adsorption (PSA), $CO_2$ is separated from raw biogas at elevated pressure using adsorbent material. Later the adsorbed gases are desorbed by reducing the pressure. In PSA, removal of hydrogen sulphide ($H_2S$) is primary step as it is harmful for the process, and also adsorption of this gas is an irreversible process. In this process high methane concentration can be achieved (95-99%). Figure 6 shows process flow diagram of PSA [10].

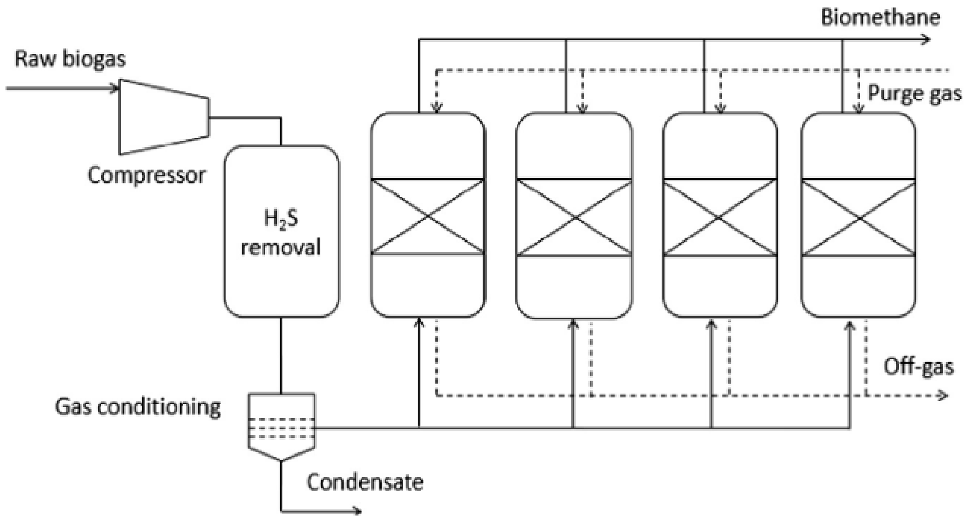


Figure 6: Process flow diagram of pressure swing adsorption [10].

### 3.4 CHEMICAL SCRUBBING (CS)

Chemical scrubbing (chemical absorption) is capable of producing gas with higher methane content greater than 95%, with no methane losses. Hence, this technique is widely used. Various chemicals are used as absorbents for absorbing $CO_2$. These chemicals can be alkaline solutions, amine solutions, ionic liquids, ammonia [3]. Advantages and disadvantages of some commonly used chemicals are given in Table 2 [3]. As shown in the table, Amine solutions have highest removal efficiency with low costs. Hence, they are commonly used compared to other two. Typically, an amine chemical scrubber system consists of an absorber, which absorbs $CO_2$ from the biogas and stripper which further separates $CO_2$ from the waste solution by heating under pressure. The raw biogas enters the absorber from the bottom and the amine solution enters from the top, to achieve a counter current flow for the two solutions. The $CO_2$ from the biogas is absorber by the amine solutions and treated biomethane ($CH_4$) is collected from the top outlet of the absorber. This is an exothermic reaction, which increases the system temperature by almost 20-25°C. Generally, the solubility of $CO_2$ decreases with increase in temperature, but in amine solution the solubility increases as the temperature increases, this gives more absorption of $CO_2$. The liquid from the bottom of the absorber is passed through reboiler to the top if stripping column, where it is connected with steam and $CO_2$ is released [10]. Figure 7 shows the process flow diagram of amine scrubber [10].

Table 2: Advantages and disadvantages of different chemicals [3].

| Chemicals | Advantages | Disadvantages |
|---|---|---|
| Ammonia | High $CO_2$ loading capacity.<br>No solvent degradation. | High volatility.<br>Low $CO_2$ absorption rate.<br>Solvent slippage. |
| NaOH | Low electricity requirement.<br>Low $CH_4$ losses. | Expensive operation and investment.<br>Requires high heat for regeneration. |
| Amines | High efficiency.<br>Cheap operation.<br>High $CO_2$/vol absorption. | Expensive investment and corrosion possibility.<br>Requires high heat for regeneration.<br>Precipitation of salts and possibility of foaming. |

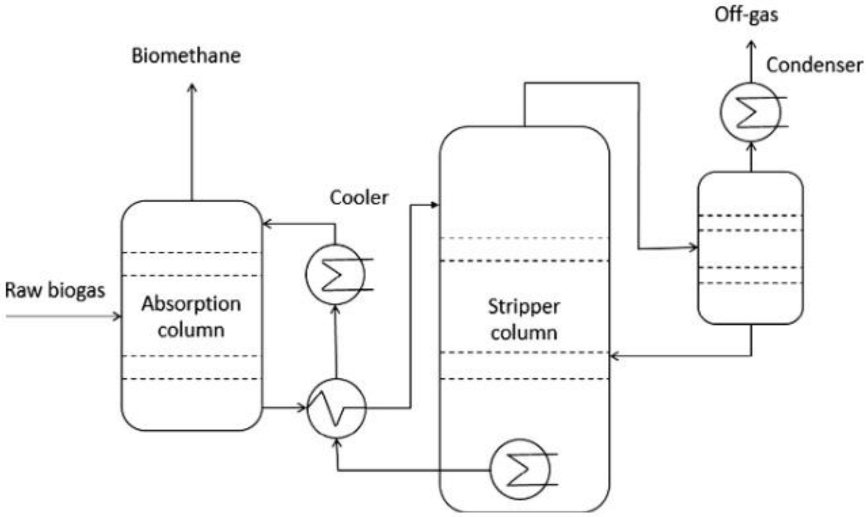


Figure 7: Process flow diagram of amine scrubber [10].

# 4. DISCUSSION

## 4.1 MEMBRANE SEPARATION (MS)

Membrane separation (MS) is a cheap process with low operation and investment cost, less demand for energy. It requires single and compact membrane equipment setup. Polymeric, inorganic and mixed matrix membranes used for biogas purification.

Polymeric membranes have excellent mechanical strength and they are easy to fabricate with low cost, and high selective permeation. Cellulose acetate (CA) and polyimide (PI) are commonly used commercial membranes for biogas separation.

Inorganic membranes are more advantageous than conventional polymeric membranes as they have more mechanical strength, thermal stability, and resistance against chemicals. Mostly inorganic membranes show good permeability and selectivity. Some inorganic membranes are zeolite, activated carbon, silica, carbon nanotubes (CNT) and metal organic framework (MOF).

## 4.2 HIGH PRESSURE WATER SCRUBBING (HPWS)

HPWS is an environment friendly process, with higher stability and safety [8]. The liquid/gas ratio, pressure, temperature, $CO_2$ content are important parameters for $CO_2$ removal in biogas. According to Y. Xiao et al. [8] $CO_2$ removal ratio was increased from 34.6% to 94.2% as liquid/gas ratio increased from 0.14 to 0.50. High pressure improves $CO_2$ removal rate. Low temperature is beneficial for more $CO_2$ removal. $CO_2$ removal ratio could reach 24.4%-83.2% with $CO_2$ content of 25%-45%. The lowest $CO_2$ content after absorption could reach 2.6% at 1.2 MPa with 400 L·h-1 gas flow and 200 L·h-1 waterflow, which meets the requirement of CO2content in natural gas for vehicle fuel. According to Ullah Khan et al. [10] HPWS gives high methane recovery (>97%). High investment and operational costs are required, also energy demand is very high during water regeneration which leads to high costs.

## 4.3 PRESSURE SWING ADSORPTION (PSA)

According to Ullah Khan et al. [10] Pressure swing adsorption yield high concentrated methane gas (95-99%). Also, this process needs extensive process control system and higher investment and operational costs. Impurities in raw biogas streams affect the overall $CO_2$ removal efficiency. The adsorbent material selection for the PSA process is very important to achieve high selectivity of $CO_2$. Commonly used adsorbent materials for biogas upgrading are molecular sieve zeolites and activated carbon. PSA process has a low energy demand [10].

## 4.4 CHEMICAL SCRUBBING (CS)

Amine sorbents are more advantageous than other chemicals used in CS. The amine sorbents may reduce the sensible heat when switching between adsorption and desorption, since the heat capacities of the solids are lower than that of liquids and hence water evaporation can also be avoided. Emissions for the degraded products and also corrosion can be minimized due to the immobilization of the amine sorbents. It becomes easier to operate gas/solid system for small scale applications compared to gas/liquid system [5]. Maile et al. carried out a chemical scrubbing test for biogas purification using ammonia as an absorbent, According to Maile et al. [1] increase in absorbent concentration increased the removal efficiency as the reacting ions in solution increases. Raw biogas with 54% $CH_4$ vol was improved to 83% vol after absorption. $CO_2$ removal efficiency was increased from 22% to 66%. Also, absorption rate depends upon the temperature, it increased with an increase in the temperature. The removal efficiency for $NH_3$ increased from 69%-79% on average with $CH_4$ concentration reaching up to 85% vol, which is equivalent to a calorific value of 22-33.5 MJ/Nm$^3$, which can be used in automobile engines.

Table 3: Advantages and disadvantages of biogas upgrading technologies in [10].

| Technology | Advantages | Disadvantages |
|---|---|---|
| MS | Less operational and capital investment costs and high $CH_4$ recovery up to > 96%.<br>Small space requirements and available at low capacities.<br>Easy maintenance without hazardous chemicals.<br>Low maintenance cost<br>Simple and environmentally friendly process | For high purity product, multiple steps of membrane are required.<br>Low $CH_4$ yield in single step.<br>Low membrane selectivity<br>Not suitable for high purity needs.<br>Consumes more electricity per unit of gas produced. |
| HPWS | > 97% $CH_4$ concentration.<br>Removal of both $CO_2$ and $H_2S$.<br>No special handling and chemicals are required.<br>Easy in operation with low $CH_4$ loses (< 2%). | High investment and operating costs.<br>Less efficient.<br>Low flexibility toward variation of input gas.<br>Slow process. |

| | | |
|---|---|---|
| | Tolerant for impurities<br>Regeneration of water is possible | High pressure, need higher energy to compress the gas and to pump water.<br>Clogging due to bacterial growth.<br>Corrosion problem due to $H_2S$. |
| PSA | 95–99% $CH_4$ concentration.<br>The humidity of the raw biogas can be removed.<br>Less energy demand with low emissions, elimination of nitrogen and oxygen is also possible.<br>Clean and water-free gas.<br>Relatively fast installation and easy start up. | High capital investment and operational costs (due to a number of columns in PSA unit).<br>$H_2S$ elimination step is needed and tail gas from the process needs to be treated.<br>Water should be removed before PSA process.<br>Susceptible to fouling by impurities in the biogas stream.<br>High $CH_4$ losses when valves malfunction. |
| CS | High purity of $CH_4$ with 98% concentration.<br>$CO_2$ purity is also high and can be used as a dry ice.<br>Low energy and cost are required to obtain highly pure liquefied biomethane (LBM) with less than 1% $CH_4$ loss.<br>Environmentally friendly technique with no chemicals use. | High investment, maintenance and operational costs.<br>High energy requirements.<br>Use of different expensive process equipment. |

## 5. CONCLUSION

Cost minimization should not be the only criterion while selecting a specific biogas upgrading technique, it is equally important to evaluate that whether a specific technology satisfies a specific demand. Biogas production is developed commercially but its global usage is still limited due to the stringent requirements before its usage. This survey has found that a lot of research is still needed for reduction of $CH_4$ loss, investment costs, environmental impacts and reducing the energy demand. Developed biogas upgrading technologies are water scrubbing, pressure swing adsorption, chemical scrubbing, but membrane scrubbing, due to its economic and environmental aspects can replace all the existing technologies in the near future. Biogas can be used as a substitute to natural gas in numerous applications, it can be converted to bio-CNG as an alternative to CNG used in vehicles. Bio-CNG can play an important role in minimising the environmental pollution caused due to burning of fossil fuels.

## 6. REFERENCES


[1] I. O. Maile and E. Muzenda, "Carbon dioxide removal using ammonia in biogas upgrading and purification," *Stud. Univ. Babeș-Bolyai Chem.*, vol. 62, no. 4, pp. 471–482, Dec. 2017.

[2] A. M. I. Yousef, Y. A. Eldrainy, W. M. El-Maghlany, and A. Attia, "Upgrading biogas by a low-temperature CO2 removal technique," *Alexandria Eng. J.*, vol. 55, no. 2, pp. 1143–1150, Jun. 2016.

[3] O. I. Maile, E. Muzenda, and H. Tesfagiorgis, "Chemical Absorption of Carbon Dioxide in Biogas Purification," *Procedia Manuf.*, vol. 7, pp. 639–646, Jan. 2017.

[4] G. Lorenzi, M. Gorgoroni, C. Silva, and M. Santarelli, "Life Cycle Assessment of biogas upgrading routes," *Energy Procedia*, vol. 158, pp. 2012–2018, Feb. 2019.

[5] S. Sutanto, J. W. Dijkstra, J. A. Z. Pieterse, J. Boon, P. Hauwert, and D. W. F. Brilman, "CO2 removal from biogas with supported amine sorbents: First technical evaluation based on experimental data," *Sep. Purif. Technol.*, vol. 184, pp. 12–25, Aug. 2017.

[6] E. Nutiu, "Anaerobic Purification Installation with Production of Biogas and Liquid Fertilizers," *Procedia Technol.*, vol. 12, pp. 632–636, Jan. 2014.

[7] H. Li, Y. Tan, M. Ditaranto, J. Yan, and Z. Yu, "Capturing CO2 from Biogas Plants," *Energy Procedia*, vol. 114, pp. 6030–6035, Jul. 2017.

[8] Y. Xiao *et al.*, "CO2 Removal from Biogas by Water Washing System," *Chinese J. Chem. Eng.*, vol. 22, no. 8, pp. 950–953, Aug. 2014.

[9] Y. Xiao and X. Li, "Removal of Carbon Dioxide from Biogas with Pilot Chemical Absorption System at Different Operating Conditions," *Asian J. Chem.*, vol. 26, no. 11, pp. 3204–3208, Feb. 2014.

[10] I. Ullah Khan *et al.*, "Biogas as a renewable energy fuel – A review of biogas upgrading, utilisation and storage," *Energy Convers. Manag.*, vol. 150, pp. 277–294, Oct. 2017.