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Enrichment of Biogas for Use as Vehicular Fuel: A Review of the Upgrading Techniques

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***Abstract*—** Biogas, a renewable energy, can be captured, upgraded and used to fuel a vehicle as an alternative to fossil fuel, thus, reducing greenhouse gas emission. Biogas is environmentally hazardous if emitted directly into the environment. Increasing demand for bio-methane to be used as vehicular fuel has called for efficient use of waste and technology that is optimal yet economical. Biogas in its raw state contains impurities that reduce its heating value to be used directly as fuel, hence, a need to enhance it by upgrading to bio-methane. Several techniques exist for upgrading biogas to bio-methane. This paper present four upgrading techniques; absorption, adsorption, membrane and cryogenic techniques, a brief theoretical background, advantages and operational issues associated with each technique.

***Keywords*—**Biogas, Enrichment, Vehicular fuel and Environment

I. INTRODUCTION

THE development of renewable energy has attracted a great deal of interest not only because of the steady rise in oil prices, but also because of the limit of fossil fuel reserves [1]. Bio-methane, an enriched biogas, is an important renewable fuel; it is environmentally friendly, clean, cheap and versatile [2]. Biogas is typically produced by the decomposition of organic matters in the absence of oxygen. Raw biogas comprises mainly methane and carbon dioxide, and smaller traces of the pollutant hydrogen sulphide, nitrogen and water vapour. The biogas heating power is proportional to the methane concentration. However, the proportion of methane to carbon dioxide in biogas varies to some degree depending on the composition of the substrate [3], digestion systems, temperature, and retention time [4]. Raw biogas contains about 50–65% methane (CH_4), 30–45% carbon dioxide (CO_2), traces of hydrogen sulphide and fractions of water vapour [5]. Raw biogas with methane content of 50% has a heating value of 21MJ/m^3 while upgrade biogas with methane content of 100% has a heating value of 33.41MJ/m^3 which makes upgraded biogas better suited for use in higher value applications such as vehicular fuels [4], [6]. Natural gas has 75-98% methane with small percentages of ethane, butane, propane. It is possible to improve the quality of biogas by enriching its methane content up to the natural gas level. Current technologies for upgrading biogas are often a multi-stage process. The removal of hydrogen sulphide, carbon dioxide and water from biogas often require different processes and this adds to the cost of biogas upgrading. However, the upgrading technology is rapidly evolving and becoming cheaper [7]. The gas upgrading processes for removal of carbon dioxide from gaseous process stream can generally be classified into: absorption, adsorption, cryogenic and membrane.

In sustaining the environment, all waste to energy conversion processes must be carried out in a safe and efficient manner. This is to ensure that human being and the ecosystem are protected from the negative effect of any of such conversion process. Issues such as the selection of an optimal technique for biogas upgrading, the environmental impact, efficiency, operational condition, scalability and cost implication of the chosen technique all requires critical assessment. This paper gives an overview of four biogas upgrading techniques: starting from a brief theoretical background, to a description of the state-of-the-art in terms of research and industrial applications, and operational issues associated with each technique.

II. BIOGAS ENVIRONMENTAL IMPACT

Biogas is considered an interesting fuel alternative from an environmental perspective because biogas is an environmentally hazardous by-product to traditional waste treatment methods such as landfilling of organic waste. When biogas is released to the atmosphere, the methane content, a greenhouse gas, has about 20 times the global warming potential of carbon dioxide [8]. Methane, hydrogen sulphide and siloxane present in biogas needs to be reduced to less harmful substances before been released to the environment thus the need to upgrade biogas for use as fuel. After enrichment, bio-methane when used as fuel in vehicles, offer some positive properties regarding emissions. Bio-methane creates lesser emissions when compared to other fossil fuel source like petrol and diesel. The combustion of 1kg of any hydrocarbon fuel theoretically emits about 2.7kg of carbon dioxide [9]. The fumes from petrol and diesel contain benzene and toluene which are not present in fumes from biogas [10]. Furthermore, bio-methane has lower emission of carbon monoxide, hydrocarbons, carbon dioxide, particulates and sulphide compounds as compared to diesel, petrol and natural

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gas which is valid for both light and heavy duty vehicle [10], [11].

For bio-methane to be used as fuel for internal combustion engines, it has been recommended a methane concentration greater than 90% [5]. There is currently only one standard adopted within the European Union (EU) member state for the use of biogas as a transport fuel. Sweden has a published standard - SS 15 54 38: “Motor fuels– biogas as fuel for high-speed Otto engines” [12]. The standard deals with specific characteristics relevant to the use and storage of biogas produced by anaerobic digestion for use as a motor fuel. It does not cover fuel which might be mixed with other compounds, e.g. hydrogen, propane, etc. Consequently the standard reflects a fuel with a high methane number [12]. Table I below present the specific characteristics of enriched Swedish biogas SS15 5438 [12].

III. EFFECT OF IMPURITIES IN BIOGAS ON COMBUSTION ENGINE

The impurities in biogas not only reduces the heating value of biogas it also causes damage to internal combustion engine. Carbon dioxide, hydrogen sulphide, water vapour, oxide of nitrogen and siloxane are the impurities in biogas that must be removed. Table II gives the effect of these impurities in internal combustion engine [13].

TABLE I

CHARACTERISTICS OF ENRICHED SWEDISH BIOGAS SS15 54 38 FOR USE AS VEHICULAR FUEL [12]

Property	Units	Requirement Type A	Requirement Type B
Wobbe Index	MJ/m^3	44.7-46.4	43.9-47.3
Methane (Volume at 273K, 101.3KPa)	%	97±1	97±2
Motor octane number		130	130
Dew point at highest storage pressure *t=lowest monthly daily average temp.*	^{0}C	t-5	t-5
Water content	mg/m^3	32	32
CO_2+O_2+N_2 by vol. max	%	4.0	5.0
of which O_2 max	%	1.0	1.0
Total sulphur	mg/m^3	23	23
Total nitrogen compound calculated as NH_3	mg/m^3	20	20

TABLE II

THE EFFECT OF BIO-GAS IMPURITIES WHEN USED AS FUEL ON INTERNAL COMBUSTION ENGINE [13]

Component	Content	Effect
Carbon dioxide	25-30%	• Lowers the heating value • Increases the methane number & the anti-knock properties of engines • Causes corrosion (low concentrated carbon acid) if the gas is wet • Damage alkali fuel
Hydrogen sulphide	0-0.5% by vol.	• Corrosive effect in equipment and piping system (stress corrosion), many manufacturer of engines therefore set an upper limit of 0.05 by vol. % • Sulphur dioxide emissions after burners or hydrogen sulphide emission with imperfect combustion – upper limit 0.1 by vol. % • Spoils catalyst
Ammonia	0-0.05% by vol.	• NO_x emissions after burners damage fuel cells • Increases the anti-knock properties of engines
Water vapour	1-5% by vol.	• Causes corrosion of equipment & piping systems • Condensates damage instrument & plants • Risk of freezing of piping system and nozzles
Dust	>5µm	• Block nozzles and fuel cells
Nitrogen	0.5% by vol.	• Lowers the heating value • Increase the anti-knock properties of engines
Siloxane	0-50mg/m^3	• Act like an abrasive and damage engines

IV. BIOGAS UPGRADING TECHNOLOGIES

The research into biogas enrichment can be divided into two stages, namely research in the laboratory conditions and research in operative conditions. The laboratory research is used for analysis of existing techniques, development of new technologies and prototype development. These are tested in operative conditions, if successful, they are optimized for industrial operation [14]. Upgrading adds to cost of biogas production. It is therefore important to have an optimized upgrading process in terms of low energy and material consumption with high efficiency giving high methane content in the upgraded gas. It is also very important to minimize, or if possible avoid, emissions of methane from the upgrading process. This means that the methane content in the reject gas, and impurities absorbed in any other stream leaving the upgrading plant should be reduced to less harmful product and (or) minimised [15].

Both the laboratory research and optimized industrial application requires two processes; biogas cleaning and biogas upgrading which can be referred to as biogas enrichment. The cleaning of the biogas consists of removal of corrosive products, mainly hydrogen sulphide, water and particles while the upgrading consists of removal of carbon dioxide to increase the energy level of the gas [10]. The common technique for removal of carbon dioxide can also remove other acid gases, hydrogen sulphide and trace of nitrogen from biogas to an extent. Hydrogen sulphide, carbon dioxide and sulphur dioxide are termed as acid gases since they dissociate to form a weak acidic solution when they come into contact with water or an aqueous medium [16]. In spite of this, it is often important to pre-separate some components like hydrogen sulphide if present in high level from biogas before been upgraded to bio-methane since these acidic gases can cause operational problems in the upgrading plant [10]. Hence it is necessary to briefly examine the cleaning of biogas after which the upgrading techniques will be discussed.

V. BIOGAS CLEANING

A. *Removal of hydrogen sulphide*

The removal of hydrogen sulphide could start from the digester by the addition of iron chloride to the digester slurry to precipitate out as iron sulphide and be removed together with the digestate. Hydrogen sulphide can be removed from biogas by adsorption on activated carbon. The rate of reaction can be catalysed by doping the pore of the activated carbon with potassium iodide, potassium carbonate (K_2CO_3) or zinc oxide [15]. The doping with zinc oxide it most preferred, though expensive, in its ability to removed hydrogen sulphide to less than 1ppm in biogas for use as vehicular fuel [15]. Horikawa, et. al. 2004, used iron-chelated solution catalysed by ferric ethylenediamine tetraacetic acid (Fe/EDTA) for removal hydrogen sulphide only from raw biogas. The process of chemical absorption of hydrogen sulphide into iron-chelated solutions offers a high efficiency and selectivity with low consumption of chemical because iron-chelated solutions function as a pseudo-catalyst that can be regenerated [7]. The Fe/EDTA converts hydrogen sulphide into elemental Sulphur. In the iron chelated based process, the sulphur produced is easily recoverable from the slurry by sedimentation or filtration operations and the whole process can be carried out at ambient temperature. With the selective removal of hydrogen sulphide, the biogas is highly concentrated with only carbon dioxide as impurity which can be scrubbed using amine solutions.

B. *Removal of water and other impurities*

Water can be removed from biogas by cooling, compression, adsorption using silicon dioxide (SiO_2) and activated carbon. By increasing the pressure or decreasing the temperature, water will condensate from biogas and can therefore be removed.

Particles in biogas can be removed by passing biogas over mechanical filters. Nitrogen and oxygen can be removed by adsorption with activated carbon, carbon molecular sieve or membrane [17]. No separate system is required for the removal of ammonia as it can be removed during gas drying or during biogas upgrading process. Siloxane can be removed by cooling the gas, by adsorption on activated carbon, activated aluminium or silica gel, or by absorption in liquid mixtures of hydrocarbons. Siloxane can also be removed whilst separating hydrogen sulphide during the cleaning process [15].

VI. UPGRADING TECHNIQUES

A. *Absorption*

Absorption is a diffusional operation in which some components of the gas phase are absorbed by the liquid they are in contact with. The region separating the two phases is called the interfacial region [18]. Stripping is exactly the reverse of absorption. It is the transfer of component from a liquid phase in which gas is dissolved to a gas phase. Absorption is undoubtedly the single most important operation of gas purification process and is used in a large number of systems [19]. Absorption and stripping are two process operations that normally are coupled in order to remove some minor components, the solute, from an incoming process gas stream and then recover that same component in more concentrated form. A carefully selected solvent in which the solute is selectively soluble is fed to the absorber (or Scrubber) and the rich solvent is then fed to the stripper, where the solute is recovered. This separation principle of absorption is based critically on the solubility of the solute (gas impurities) in the solvent. If an absorber is to be designed for efficient and economical service, it is critical to select the proper solvent whose attributes include availability, cost stability, volatility and non-hazardous [20]. In an upgrading plant using this technique the raw biogas is intensively contacted with a liquid within a scrubbing column filled with a plastic packing in other to increase the contact area between the phases. Because the impurities to be removed from the biogas are far more soluble in the liquid scrubbing solution than methane, they are removed from the biogas stream after which the methane rich biogas leaves the scrubbing column and the impurities are collected at the base with the scrubbing liquid. In order to maintain absorption performance, the scrubbing liquid has to be replaced by fresh liquid or regenerated in a separated step (desorption or regeneration step) [21]. There are two type of absorption processes; physical absorption process and chemical absorption process. The reaction of the solvent to the solute determines what type of absorption has taken place.

1. *Theoretical back ground and research*

Physical absorption

Physical absorption process is based critically on the solubility of the solute (gas impurities) in the solvent. Pressurised gas scrubbing using water as the absorbent is a physical absorption process. Other solvent used in the process are polyethylene glycol-dimethyl ether (PEG-DME) e.g the genosorb 1753 solvent, otherwise known as selexol, and propylene carbonate [22], [23] which are organic solvents. The absorption of carbon dioxide and methane into water is described by Henry law, as in (1), which describes the relationship between the partial pressure of a gas and the concentration of the gas in a liquid in contact with the gas [24].

$$C_A(M) = K_H(M/atm) * P_A(atm) \qquad (1)$$

In (1), C_A is the concentration of A in the liquid-phase, K_H is Henry's constant and P_A is the partial pressure of A. The Henry constant at 25°C (K_H) for carbon dioxide is $3.4*10^{-2}$ M/atm and for methane $1.3*10^{-3}$ M/atm, resulting in a solubility for carbon dioxide that is approximately 26 times higher than for methane [24], [25]. The value of Henry's constant for a specific gas is only valid at one specific temperature [24]. When the temperature is increased, the solubility usually decreases and vice versa [24]. The amount of water needed to remove a certain amount of carbon dioxide depends on the design of the column, the required carbon dioxide concentration in the upgraded biogas and the solubility of carbon dioxide in a certain volume of water (determined by the pressure and the temperature) [25]. Solubility of carbon dioxide and hydrogen sulphide in water as compared to methane as well as the low cost of water has made the water scrubbing technique the simplest for biogas upgrading in some countries allowing for 98% methane purity [26]. With a specific design and a specified carbon dioxide concentration in the upgraded biogas, the water flow rate and the gas composition will be determined by the solubility of carbon dioxide in water [25]. Equation (2) and (3) gives the water flow rate required to remove carbon dioxide from biogas [25].

$$Q_{water}(l/h) = \frac{Q_{CO_2}(g)(mol/h)}{C_{CO_2}(aq)(M)} \tag{2}$$

$$Q_{water}(l/h) = \frac{Q_{biogas} * \%CO_2(mol/h)}{K_H * P_{tot} * \%CO_2(M)} \tag{3}$$

Where Q_{water} is the required water flow, Q_{CO_2} is the molar flow of carbon dioxide that shall be removed and C_{CO_2} is the solubility of carbon dioxide described as the maximum concentration possible to reach in water. Q_{biogas} is the total biogas flow, $\%CO_2$ is the percentage of carbon dioxide in the raw biogas and P_{tot} is the pressure in the absorption column and K_H is Henry constant.

Virendra et. al 2006, demonstrated biogas purification using water as a scrubbing agent. The diameter of the scrubber and packaged height were given as 150mm and 3500mm respectively. The inlet gas flow rate was varied from 1.0-3.0m^3/h at a constant pressure of 1.0 MPa. The dissolubility of hydrogen sulphide and carbon dioxide increases with pressure, so also the saturation pressure, hence when higher pressures are reached the dissolubility of the components will not linearly increase with the pressure [7]. It was found that the percentage carbon dioxide absorption from raw biogas initially increased when the flow rate vary from 1.0 to 1.5m^3/h and afterwards it decreased continuously. The highest carbon dioxide absorption observed was 99% at 1.5m^3/h gas flow rate at 1.0 MPa inlet gas pressure. Flooding of the scrubber column was reported at 1.8m^3/h inlet flow rate of the water (Virendra K. Vijay, 2006).

Boateng and Kwofie, 2009, carried out a feasibility study on Appolonia biogas plant in Ghana, which uses water as its scrubbing agent. 95% bio-methane was recorded as the highest purity the system could deliver operating at 70% efficiency. The heating value of the raw biogas was 20MJ/m^3 and after upgrading, the heating value rose up to 28.7%MJ/m^3. In both Virendra and Boateng experiments, there was no regeneration of water laden with carbon dioxide and hydrogen sulphide; this is not an environmentally friendly practice. Regenerated water can be fed back into the scrubbing column and used again. Regeneration is accomplished by de-pressuring or by stripping with air in a similar column [27]. Stripping with air is not recommended when high level of hydrogen sulphide are contained in the biogas since water quickly become contaminated with elemental sulphur which causes operational problem and blocking of column [22] , [27].

Chemical absorption

Chemical absorption process is based on the reactivity of the chemical reagent used as absorbent to chemically react with the carbon dioxide molecule and thus removing it from the biogas feed stream. This is most commonly performed using a solution of amines (molecules with carbon and nitrogen), with the reaction product being either in the molecular or ion form [25]. Chemical scrubbing has an advantage over physical scrubbing in its capacity to absorb more carbon dioxide [22]. Alkaline and alkanolamine are among the popular reagents for practical applications of carbon dioxide and hydrogen sulphide absorption [28]. The aqueous solutions include sodium hydroxide, calcium hydroxide and potassium hydroxide. The types of amine compounds used are: mono-ethanolamine (MEA), di-methyl ethanolamine (DMEA), di-ethanol amine (DEA), deglycol amine (DGA) and diisopropanol amine (DIPA) [29]. Recently, the most common amine system used industrially today is a mixture of MDEA and piperazine (PZ) often termed activated MDEA (aMDEA) [25]. In the design of an amine based absorption scrubber, two design approaches are used; the equilibrium based approach and the rate base approach. The equilibrium base approach is suitable for non-reactive system while the rate base approach is suitable for reactive system, although most researchers use the rate base approach because of its simplicity and accuracy [30]. Amine based absorption system is a selective process, in processes for total gas impurities removal, treated gas quality is completely determined by phase equilibrium provided the column contains enough trays or packed depth. This is not the case in selective treating. The extent to which each gas impurities are removed is related directly to its mass transfer rates as well as to the mass transfer rates of each of the other absorbing acid-gas species [31]. The reaction of hydrogen sulphide with amines is essentially instantaneous and that of carbon dioxide with amine is relatively slower [31]. Therefore, for amine, hydrogen sulphide and carbon dioxide absorption in a packed column, mass transfer is not limited by chemical reaction but by the mechanical diffusion or mixing of the gas with the liquid and by the absorbing capacity of the amine [32].

Cekanova et. al. 2011, carried out an experimental laboratory research on biogas enrichment to bio-methane using chemical adsorption for removal of hydrogen sulphide and chemical absorption for removal of carbon dioxide in a scrubbing unit. Amine solution was used as the chemical solvent for scrubbing in the enrichment design. Hydrogen sulphide was removed with chemical adsorption method through the system of filters with activated carbon. Methyl-diethanolamine (MDEA) and mono-ethanolamine (MEA) solutions were used as the solvent for removal of carbon dioxide. The result of the two experiments showed that using 10% mono-ethanolamine as an absorbent resulted in 100% carbon dioxide removal in first minute of the reaction. 100%

removal was only achieved before the amine solution approaches carbon dioxide saturation, which took about 7 minutes. The reaction was exothermic and loss of the absorbent was noticed due to evapouration. Huertas et. al. 2011 used mono-ethanolamine (MEA) as the scrubbing liquid in his experiment. He reported 7.5% effectiveness of mono-ethanolamine if hydrogen sulphide is the main impurity to be removed and above 50% if carbon dioxide is the main impurity to be removed using mono-ethanolamine. Also the efficiency of the amine reduced after regeneration. He therefore recommended the removal of hydrogen sulphide before amine scrubbing is used for upgrading of biogas.

2. *Advantages of absorption*

i. Physical absorption requires less material.
ii. If impurities concentration is low they can be removed to an extent by the process [8].
iii. Biomethane stream produced by the process can be directly utilized at delivery pressure but must be compressed for use as vehicular fuel.
iv. Complete carbon dioxide removal using amine is achievable.
v. The process is highly efficient at optimal operating condition [8].
vi. It is a proven technology.

3. *Operational problems*

i. Alkali aqueous solutions are not regenerable, therefore large volume of the solvent is required
ii. Alkanolamines are regenerable but at high temperature with loss of amine after regeneration.
iii. Fluctuation in efficiency of the absorbent due to refilling of lost amine
iv. Corrosion of scrubbing column.
v. Microbial growth in the column when water is used as absorbent.
vi. Foaming can also occur when the flow rate of absorbent is not properly regulated and when impurities are present in water.
vii. Disposal of waste water [8].

B. *Adsorption*

Adsorption is the selective concentration of one or more components of a gas at the surface of a micro-porous solid, preferably one with a large surface area per unit mass [19], [33]. The mixture of adsorbed component, in this case raw biogas, is called the adsorbate and the micro-porous solid, which could be an activated carbon or zeolite, is the adsorbent. Pressure swing adsorption and temperature swing adsorption are two types of adsorption processes [33] but of importance is the pressure swing adsorption. When the regeneration of the adsorbent is performed by reducing the total pressure of the system, the process is termed pressure swing adsorption (PSA), the total pressure of the system "swings" between high pressure in feed and low pressure in regeneration [33]. Pressure swing adsorption (PSA) is a dry method used to separate gases via physical properties [25]. With the PSA technique, carbon dioxide is separated from the biogas by adsorption on a surface under elevated pressure. The adsorbing material is regenerated by a sequential decrease in pressure because the attractive forces holding the adsorbate on the adsorbent are weaker than those of the chemical bonds and the adsorbate can generally be released before the column is reloaded again, hence the name of the technique [34]. The adsorption of hydrogen sulphide is normally irreversible in the adsorbents and thus a process to eliminate this gas should be placed before the PSA [35], [36]. For a continuous production, several columns are needed as they will be closed and opened consecutively. The gas pressure released from one vessel is subsequently used by the others [34]. PSA unit characteristics include feeding pressure, purging pressure, adsorbent, cycle time and column interconnectedness [25].

1. *Theoretical back-ground and research*

The choice of adsorbent, the bed material which selectively adsorbs carbon dioxide from the raw gas stream, is crucial for the function of the PSA unit [25]. The common adsorbent materials used are activated carbon, natural and synthetic zeolites, silica gels, carbon molecular sieves (CMS) and metal organic framework, a new type of adsorbent material [25], [33]. The molecular size of methane and carbon dioxide are 3.8Å and 3.4Å respectively [36]. Therefore an adsorbent with pore matrix of 3.7Å when selected will retain most carbon dioxide until it is saturated whilst methane is not allowed to enter into the material but passes through interstitial spaces. Generally, adsorbents are one of two types; equilibrium adsorbents (activated carbons, zeolites) which have the capacity to adsorb much more carbon dioxide than methane, while kinetic adsorbents (CMS) have micro-pores which the small carbon dioxide molecules can penetrate faster than the hydrocarbons which thus pass the column bed unrestrained [25]. The correlation between gas adsorption and pressure for two adsorbent materials is shown by the isotherm diagram in fig. 1 [35].

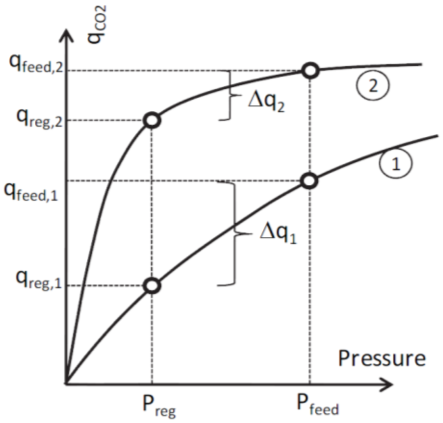

Fig. 1- Isotherm diagram for two adsorbent materials

In both materials, the adsorbent may take carbon dioxide up to the loading established by its partial pressure in the feed step (P_{feed}) which is q_{feed1} and q_{feed2} for adsorbent 1&2 respectively. Once equilibrium is reached i.e. adsorbent is saturated, it is regenerated at a lower pressure, P_{reg}, where the loading of carbon dioxide is decreased to q_{reg1} and q_{reg2}. Δq equals the amount of carbon dioxide that has been separated from the raw gas stream during this process cycle, that is, the difference between q_{feed} and q_{reg}. Adsorbent (2) has the capacity to adsorb much more carbon dioxide at P_{feed} but adsorbent (1) is the preferred choice for this process since Δq_1 is much larger than Δq_2. Therefore, when designing a PSA the isotherm shape of the adsorbent material should to be known. A good adsorbent has a nearly linear isotherm, as a curve with a low steep makes it easy to desorb the carbon dioxide at a very low pressure and low energy consumption which ensures an efficient separation process [35].

Cekanova et. al., Horikawa et. al. and Farooq et. al. have all employed this technique alongside other techniques for biogas purification though at different experimental conditions. Grande et. al. 2006, studied the adsorption of carbon dioxide on zeolite 13X an example of equilibrium adsorbent and carbon molecular sieve (CMS-3K) an example of kinetic adsorbent. It was reported that carbon molecular sieve could produce fuel grade methane with 98% purity from a 55% methane content raw biogas. For zeolite 13X, the recovery of methane was not higher than 60%. The kinetic adsorbent CMS-3K showed a good trade-off between purity and recovery and also consume less power than zeolite [37].

2. *Advantages*

i. The process of PSA requires less heat [33].
ii. There is flexibility of design and more than one absorbent can be used in the process [33], [36].
iii. It is suitable for small to medium scale plants.
iv. PSA technology does not require any water and does not produce contaminated waste water as well [25].
v. No bacteria contaminant of off-gas [8].
vi. PSA is a dry process and there is no use of liquid chemical [8].

3. *Operational issues*

The electricity consumption of a PSA system is high. To extend the operational life of the plant, hydrogen sulphide must be removed before biogas enters the adsorption chamber. Also due to the high operating pressure, cooling system is required for the compressor.

C. *Membrane separation*

Membranes are discrete, thin semi-permeable barriers that selectively separate some compounds from others [38]. Polymeric membranes separate gases by selective permeation of one or more gaseous components from one side of a membrane barrier to other side. The membrane does not operate as a filter, where small molecules are separated from larges ones through a medium of pores, rather the components dissolve in the polymer at one surface and are transported/diffuse across the membrane as the result of a concentration gradient [19], [38]. The concentration gradient is maintained by a high partial pressure of the key component in the gas on one side of the membrane barrier and a low partial pressure on the other side [19]. Two classes of membranes are used commercially in gas separation technology: The first class are glass polymer membranes which separate gases based on differences in the size of the gas molecules and the second class are membranes made either from highly flexible rubbery polymers or ultra-high free volume glassy substituted polyacetylenes which separate gases based on difference in the solubility of gas molecules in these polymers [39]. The commercially viable membranes used for carbon dioxide removal are polymer based e.g. cellulose acetate, ployimide, polyamides, polysulfone, poly carbonate and polyetherimide [38]. Membrane used for biogas upgrading allows the carbon dioxide to diffuse through it while methane is retained [25]. This results in enriched biogas that can be used to fuel a vehicle.

Raw biogas should be cleaned by removing impurities such as hydrogen sulphide, water, ammonia, siloxane and volatile organic compound before the biogas upgrading process using membrane [25]. Research into membrane material is leading the way for some of these impurities to permeate through the membrane for example a company called UOP in Illinois, United State of America designed a cellulose acetate membrane for bulk removal of hydrogen sulphide at high pressure. In high concentration of hydrogen sulphide in the biogas, most polymers tend to have little resistance to hydrogen sulphide plasticization (softening of the membrane) and thus limiting the use of membrane if the concentration of hydrogen sulphide in biogas is not known or the raw biogas composition fluctuates [38]. Since hydrogen sulphide permeates through the membrane to some extent, thus enriched biogas can still contain hydrogen sulphide [25].

1. *Theoretical Background and Research Review*

A field stream of biogas separated using membrane is split into two product stream: permeate and retentate. The permeate is the material that has passed through the membrane and the retentate is the material that has been rejected by the membrane [40]. Membrane technology can be applied to particle-liquid separation, liquid-liquid separation and gases separation [40]. The potential application of a polymer as a separation membrane depends upon the selectivity towards the gas to be separated which determines product purity and recovery and the permeate flux that determines how efficient the membrane will be [39]. The accurate design and optimization of a gas separation system using polymer membrane depends on the possibility of predicting correctly the membrane transport properties. The transport of a gas molecule through a membrane can be expressed as given in (4) [41].

$$j_i = \frac{D_i K_i \Delta P_i}{l} \tag{4}$$

In the equation j_i denotes the molar flux for gas, D_i is the permeate diffusion coefficient, K_i is the sorption coefficient, Δp_i is the difference in partial pressure between the feed and permeate side and l is the membrane thickness. The permeability of a membrane is defined as the product of the diffusion and sorption coefficient [25]. The membrane selectivity of two gases ‘a’ and ‘b’ is defined as the permeability of gas ‘a’ divided by permeability of gas ‘b’ which coefficient, sorption or diffusion depends on the type of material that is used in the membrane [25]. The permeability decreases with increasing size of the molecule in a glassy polymer which is commonly used in the membrane for biogas upgrading since diffusion coefficient is dominating [41].

Miltner et. al. 2008, reported the presence of hydrogen sulphide, ammonia and water vapour can jeopardize the membrane material hence, he recommended pre-treatment of biogas before upgrading. These pre-treatment include the drying of biogas by cooling and refrigeration method and the desulphurization over iron oxide. The biogas upgrading plant in Margarethen lower Austria produces 25kg/h (33Nm^3/h) biomethane using the membrane separation technique. Varying raw biogas composition of 40-52% vol. methane, 1 to 19ppm hydrogen sulphide is fed into the biogas upgrading plant which is fully automated. The hydrogen sulphide is removed separately while the cleaned biogas is upgraded using the membrane technique. The required quality of upgraded biogas, >95%vol. methane was satisfied within 5-10 minutes of the process start-up and was constantly delivered thereafter [42].

2. *Advantages of membrane separation technique*

The advantages of membrane technique are listed below [38]

i. Lower capital cost as compared to PSA upgrading technique.
ii. Operational simplicity and high reliability on upgrade biogas.
iii. Space optimization and compactness of the design [8].
iv. The technique is environmentally friendly as there is no waste solvent, permeate gas can be flared or used as fuel for heat engines.
v. The technique is ideal for remote location once designed and install.
vi. Absence of moving parts leads to low level mechanical wear.
vii. Low maintenance level.
viii. It is a dry process and does not require any chemical [8].

3. *Operational issue*

Exposure to certain solutions and materials causes membrane blockage or damage [6]. If proper pre-treatment is not carried out, the presence of hydrogen sulphide will lead to plasticization of the membrane material thus hampering the upgrading process. The membrane resistance to breaking due to the pressure gradient is also an important technical limitation of this technology since replacement of damage membrane is expensive [6]. Also there is need for replacement of the membrane over a specific period of time depending on the manufacturer’s specification. Energy consumption of membrane plant is normally determined by the compressor requirement [25]. The installed membrane area determines the operating pressure of the system. If the membrane area is large, lower pressure is required for the system since lower flux (permeate flow per membrane area) can be accepted [25] with reference to (4) above.

D. *Cryogenic separation*

Cryogenic separation uses the different temperature related properties of the gas species to separate them from each other [6]. The process starts with compression of raw biogas to 17-26bar and then cooled to -26^{0}C for removal of hydrogen sulphide, sulphur dioxide, halogens and siloxane [15]. The raw biogas is cooled down step wisely to temperature where carbon dioxide in the gas can be liquefied and separated through several heat exchangers [6], [15]. Pure carbon dioxide has a de-sublimation temperature of -78.5^{0}C at atmospheric pressure while methane condenses at -161^{0}C [6]. Carbon dioxide both sublimate and de-sublimate at atmospheric pressure i.e. its change state from gas to solid without going through the liquid state and the opposite (de-sublimate) without first liquefying. When carbon dioxide in biogas is de-sublimated it follows that the partial pressure of carbon dioxide is reduced, therefore the concentration of carbon dioxide is lowered and a lower temperature will be required to further de-sublimate the carbon dioxide [6]. Depending on the temperature of the process different purity can be reached. A lower temperature results in a higher removal efficiency of carbon dioxide. However, the presence of methane in the biogas mixture affects the characteristics of the gas thus requiring higher pressure and\or lower temperature to condense carbon dioxide [15]. To avoid freezing and other problems in cryogenic process, water and hydrogen sulphide need to be removed [17].

1. *Theoretical background*

The cryogenic process is basically to generate low temperature for the de-sublimation of carbon dioxide from biogas. Cooling can be achieved directly or indirectly. Direct cooling can be achieved with a combination of equipment such as compressor, heat exchanger and expansion device just as used in the refrigeration system for refrigerant cooling. The indirect cooling is by a heat exchanger with liquid nitrogen to liquefy the biogas. This indirect cooling is not viable on a large scale because of the running cost as the introduced nitrogen is consumed in the process. The two main working process cycle of the cooling system as used in the cryogenic biogas upgrading are open loop process cycle and the closed loop process cycle [43].

Open loop process cycle

Biogas is first compressed to a high pressure causing a rise in temperature. This creates a good physical property for the biogas to be heat exchanged with lower temperature heat sink e.g a refrigeration cycle. After the biogas has been cooled, it is expanded through a turbine where the pressure and temperature are decreased. The biogas can this way reach a low enough temperature to begin the de-sublimation of carbon dioxide [43].

Closed loop process cycle

Biogas is not compressed before been heat exchanged thus resulting in lower temperature difference between the biogas stream and the heat exchanger medium. Since the biogas temperature is not increased via compression, it is not possible to use the air as a heat sink therefore a cooling agent e.g. nitrogen and methane or a mixture of both is required. The biogas is cooled by the cooling agent before expansion in a turbine. This decreases both the pressure and temperature which leads to the sublimation of carbon dioxide [43].

The main part of heat transfer between the biogas and the cooling media is through convection. A decrease in the temperature of the biogas will result in increase in viscosity and density and a decrease in diffusivity within the biogas. Thus the flow velocity decreases due to increased density [6]. The mass flow of carbon dioxide decreases along the heat exchanger length as the temperature decreases. The heat exchangers ability to separate carbon dioxide from biogas is dependent on the mass flow rate of the incoming biogas, the concentration of carbon dioxide in the biogas and the temperature of the incoming cooling media. Also the geometric properties of the heat exchanger e.g. total heat exchanger area, size of plate and number of plates, contribute to the functionality of the heat exchanger [6].

Cryogenic technique is relatively new as reported in many literatures for upgrading of biogas but some few companies are already deploying it at pilot plant stages. Gastreatment services B.V from The Netherlands, Scandinavian Gts, Acrion Technologies and Prometheus-Energy are some of the companies offering services with this technology.

2. *Advantages of Cryogenic techniques*

i. It does not require water or any absorbent to remove impurities. No chemical contact is made with the biogas.
ii. It can be used to produce high grade quality methane without reacting with any of the compounds in the biogas
iii. The process can be used to produce liquefied biogas which occupies less space as compared to compressed biogas [43].
iv. Upgraded biogas produced with this technique is already at an elevated pressure and does not need further compression to be used as vehicular fuel.
v. Also solid carbon dioxide could be produce in the process [6].
vi. Cryogenic technology is suitable for upgrading of landfill gas since nitrogen gas can be separated in the methane liquefaction step [43].

3. *Operational problem*

i. High pressure and low temperature is required for this process.
ii. Adequate insulation is required to prevent heat from the surrounding.
iii. The electricity demand ranges from 0.63-1.8kWh electricity per Nm^3 of biogas for upgrading which is not energy efficient [6], [25].
iv. The frost layer produced by carbon dioxide has a consequence in the heat exchanger ability to further separate carbon dioxide from the biogas [6].

VII. COMPARISON OF THE BIOGAS UPGRADING TECHNIQUES

Table III provides a comparison of four upgrading techniques discussed. The upgrading techniques will be compared based on;

i. Gas purity produced- The capability of each technique to remove carbon dioxide from the inlet biogas and increase the concentration of the methane.
ii. Process requirement- Water, chemicals, electrical power and heat
iii. Methane slip – the methane content that can be lost during the upgrading process
iv. Hydrogen sulphide separation – the need to pre-treat the biogas before upgrading.
v. Gas compression need for use as vehicular fuel.

TABLE III
COMPARISON OF FOUR UPGRADING TECHNIQUES

Separation technique	Gas purity (methane conc.)	Methane slip	Pre-treatment required prior to upgrading	Gas compression required prior to utilization as vehicular fuel	Process requirements	Electricity demand (kWh/m^3 BG)	Off-gas treatment [44]	Cost [8]	Operational plant reference [15]
Physical absorption (water)	>98% [25], >96-98% [6], 98-99.5% [44]	Flow through scrubber 2% [6], 1% [25]	Yes	Yes	Large volume of water required. Refill of anti-foaming agent	0.2-0.3 [44] 0.4-0.5 [6]	Yes	Medium	Very high
Physical absorption (organic)	96-99%, 96-99% [44]	1-4%	Yes	Yes	Refill of absorbent	0.23-0.33 [44] 0.10-0.15 [25]	Yes	Medium	Low
Chemical absorption (amines)	>99.8% [25], >99.5% [6], ~99.9% [44]	0.1% [25], 0.1-0.2% Amine react only with CO_2 [6]	Yes	Yes	Refill of amines [6]	0.06-0.17 [6] 0.05-0.18 [25]	No	High	High
Adsorption (PSA)	>98% [25], 95-98% [6], 90-98.5% [44]	2% [6], 1.8-2% [25]	Yes	Yes	Nil	0.16-0.35 [44] 0.29-0.43 [6]	Yes	Medium	Very high
Membrane	98% [25], [6], 85-99% [44]	2% [6], 0.5% [25]	Yes	Yes	Replacement of membrane	0.18-0.35 [44] 0.26 [6] 0.20-0.30 [25]	Yes	High	Low
Cryogenic	99.99% [45],		Yes	No		0.18-0.25 [44]	No	High	Pilot plant

separation	>97% [6], 98-99.9% [44]	0.42-0.63 [6]	only

Of the four processes only chemical absorption requires a substantial amount of heat for the regeneration of the amines [6]. The electricity demand for cryogenic is very high at about 0.63kWh/m^3 upgraded biogas while that of pressure swing adsorption is about 0.5-0.6kWh/m^3 upgraded biogas [6], [25]. All technologies require compression except cryogenic separation for the upgraded biogas to be used as vehicular fuel. The energy required to compress the gas depends on the volume of the gas that is to be compressed, the inlet temperature of the gas, the ratio of specific heat (C_p/C_v) for the gas, inlet and outlet pressure and the efficiency of the compressor. The ratio of specific heat is the only parameter that depends on the composition of the biogas. C_p/C_v equals 1.307 and 1.304 for methane and carbon dioxide respectively at 15^{0}C & 1 atm [25].

VIII. CONCLUSION

The biogas enrichment techniques reviewed in this paper shows effectiveness in upgrading biogas to quality biomethane for use as vehicular fuel. Absorption, Adsorption and Membrane techniques with lots of technical expertise and operational data can be deployed for upgrading biogas after a careful evaluation of the investment cost. The investment cost depends on the scale of the project but from literatures, physical absorption and pressure swing adsorption has the least investment cost over a large scale production level. Cryogenic technique is still in its early stage of implementation and would not be recommended for full scale deployment. Upgraded biogas when used as fuel provides much benefit to the ecosystem by reducing greenhouse gas emission and ensuring a more sustainable environment.

REFERENCES

[1] C. M. Drapcho, N. P. Nhuan and T. H. Walker, Biofuels Engineering Process Technology, McGraw Hill, 2008.

[2] V. K. Vijay, R. Chandra and P. M. V. Subbarao, "Vehicular Quality Biomethane Production from Biogas by Using Automated Water Scrubbing System," *International Scholarly Research network, ISRN Renewable Energy,* vol. 2012, p. 6, 2012.

[3] O. C. Boateng and E. M. Kwofie, "Water Scrubbing: A Better Option for biogas Purification for Effective Storage," *World Applied Sciences Journal 5(Special Issue for Environment),* pp. 122-125, 2009.

[4] T. Al Seadi, D. Rutz, H. Prassl, M. Kottner, T. Finsterwalder, S. Volk and R. Janssen, Biogas Handbook, T. Al Seadi, Ed., Denmark, Esbjerg: University of Southern Denmark, 2008.

[5] P. O. G. Z.-T. A. C. M. Harasimowicz, "Application of polyimide membranes for biogas purification and enrichment," *Journal of hazardous Material,* vol. 144, no. 3, pp. 698-702, 18 june 2007.

[6] S. Jonsson and J. Westman, "Cryogenic Biogas Upgrading Using Plate Heat Exchangers," Chalmers University of Technology, Goteborg, Sweden, 2011.

[7] J. C. Reijenga, L. Bini, J. I. Maassen, P. A. Van Meel, J. De Hullu, S. Shazad and J. M. Vaessen, "Comparing Different Biogas Upgrading Techniques: Interim Report," Eindhoven University of Technology, 2008.

[8] E. Dirkse, "Biogas Upgrading Using the DMT TS-PWS Technology," DMT Environmental Technology, 2008.

[9] G. M. K. Babu and K. A. Subramanian, Alternative Transportation Fuels: Utilisation in Combustion Engines, Boca Raton: CRC Press, Taylor & Francis Group, 2013.

[10] M. Persson, "Evaluation of Upgrading Technique for Biogas," swedish Gas Center, Lund, 2003.

[11] R. C. P. M. V. S. a. S. S. K. Virendra K. Vijay, "Biogas Purification and Bottling into CNG Cylinders: Producing Bio-CNG from Biomass for Rural Automotive Applications," in *The 2nd Joint International Conference on 'Sustainable Energy and Environment (SEE 2006)',* Bangkok, Thailand, 2006.

[12] Sustainable Transport Group, "Biogas as Road Transport Fuel: An Assessment of the Potential Role of Biogas as a Renewable Transport Fuel," NSCA, England, 2006.

[13] D. Deublein and A. Steinhauser, Biogas from waste & Renewable Resources: An Introduction, Weinheim: Wiley-VCH, 2008.

[14] P. Cekanova, N. Jasminska, T. Brestovic and E. Schvarzbacherova, "Biogas Upgrading Processess for the production of Natural gas substitute," *The Holistic Approach to Environment,* pp. 53-62, 24 05 2011.

[15] A. Petersson and A. Wellinger, "Biogas Upgrading Technologies-Developments & Innovation," IEA Bioenergy, 2009.

[16] B. Shimekit and H. Mukhtar, "Natural Gas Purification Technologies - Major Advances for CO2 Separation and Future Directions," in *Advances in Natural Gas Technology,* H. Dr. Al-Megren, Ed., InTech, 2012, pp. 237-270.

[17] M. Persson, O. Jonsson and A. Wellinger, "Biogas upgrading to Vehicle Fuel Standard and Grid Injection," IEA Bioenergy, Vienna, 2006.

[18] C. Andrzej and Z. Roman, Absorption: Fundamentals & Application, 1st ed., Pergamon Press, 1993.

[19] K. L. Arthur and N. B. Richard, Gas Purification, 5th ed., New York: Gulf Publishing Compny, 1997.

[20] F. R. James, Absorption adn Stripping; The Enginnering Hndbook, Austin: CRC PRESS LLC, 2005, p. Chapter 59.

[21] Vienna University of Technology, "Biogas to Biomethane Technology Review," Vienna, Austria, 2012.

[22] H. Nie, H. Jiang, D. Chong, Q. Wu, C. Xu and H. Zhou, "Comaprison of Water Scrubbing and Propylene Carbonate Absorption for Biogas Upgrading Process," *Energy & Fuels,* no. 27, p. 3239−3245, 13 May 2013.

[23] M. Gotz, F. Ortloff, R. Reimert, O. Basha, B. I. Morsi and T. Kolb, "Evaluation of Organic and Ionic Liquids for Three-phase Methanation and Biogas Purification Processes," *Energy & Fuels,* vol. 27, pp. 4705-4716, 27 June 2013.

[24] W. Stumm and J. J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd ed., New York: Wiley, 1996.

[25] F. Bauer, C. Hulteberg, T. Persson and D. Tamm, "Biogas upgrading - Review of commercial technologies," Svenskt Gastekniskt Center (SGC) AB, Malmö, Sweden, 2013.

[26] Y. Belmabkhout, N. Heyman, G. De Weireld and A. Sayari, "Simultaneous Adsorption of H2S and CO2 on Triamine Grafted Pore-Expanded Mesoporous MCM-41 Silica," *Energy & Fuels,* pp. 1310-1315, 04 02 2011.

[27] Q. Zhau, E. Leonhardt, C. MacConnell, C. Frear and S. Chen, "Purification Technologies for Biogas Generated by Anaerobic Digestion," *CSANR Research Report,* pp. 01-24, 2010.

[28] N. Tippayawong and P. Thanompongchart, "Biogas quality upgrade by simultaneous removal of CO2 and H2S in a Packed Column Reactor," *Energy,* pp. 1-4, 2010.

[29] V. D. Prakash and M. V. Vijaykumar, "Quickly Design CO2-Amine Absorber," *Indian Journal of Chemical Technology,* vol. 13, pp. 47-52, Januanry 2006.

[30] N. Kasiri and M. A. Ghayyem, "Rate Based Model in H2S and CO2 Absorption Column Using Alkanolamine Solutions," *IUST International Journal of Engineering Science,* vol. 19, no. 5-2, pp. 89-98, 2008.

[31] K. H. Mohamadbigy, M. Bazm, R. Behradi and R. Binesh, "Amine Absorption Column Design Using Mass Transfer Rate Simulation,"

Petroleum & Coal, vol. 47, no. 2, pp. 39-46, November 2005.

[32] J. I. Huertas, N. Giraldo and S. Izquierdo, Removal of H2S and CO2 from Biogas by Amine Absorption, Mass Transfer in Chemical Engineering Process, Vols. Automotive Engineering Research Center-CIMA of Tecnologico de Monterrey,, D. J. MarkoÅ¡, Ed., Mexico: InTech, 2011, pp. 133-150.

[33] C. A. Grande, "Advances in Pressure Swing Adsorption for Gas Separation," *International Scholarly Research Network Chemical Engineering,* vol. Volume 2012, no. Article ID 982934, p. 13, 2012.

[34] Vienna University of Technology, "Biogas to Biomethane Technology Review," Research Division Thermal Process Engineering and Simulation, Austria, 2012.

[35] C. A. Grande, "Biogas upgrading by Pressure Swing Adsorption," in *Biofuel's Engineering Process Technology*, D. M. A. D. S. Bernardes, Ed., Rijeka, InTech, 2011, pp. 66-84.

[36] T. Patterson, S. Esteves, R. Dinsdale and A. Guwy, "An Evaluation of the Policy and Techno-Economic Factors Affecting the Potential for Biogas Upgrading for Transport use in UK," *Energy Policy,* no. 39, pp. 1806-1816, 11 January 2011.

[37] C. A. Grande and A. E. Rodrigues, "Biogas to Fuel by Vacuum Pressure Swing Adsorption: Behaviour of Equilibrium and Kinetic Adsorption," *Ind. Eng. Chem. Res,* vol. 46, pp. 4595-4605, 2006.

[38] T. Cnop, D. Dortmundt and M. Schott, "Continued Development of Gas Separation membrane for Highly Sour Service," UOP LLC, Illinios, USA, 2007.

[39] E. Tocci and P. Pullumbi, "Mulit-Scale Molecular Modelling Approaches for Designing/Selecting Polymers Used for Developing Novel Membrane," in *Membrane Engineering for the Treatment of Gases: Gas Separation Problems with Membrane*, vol. Vol. 1, E. Drioli and G. Barbieri, Eds., Royal Society of Chemistry, 2011, pp. 1-28.

[40] J. I. Marriott, "Detail Modelling & Optimal Design of Membrane Separation System," University College London, London, 2001.

[41] R. W. Baker, Membrane Technology and Application, 2nd ed., Chichester: Wiley, 2004, pp. 1-15.

[42] M. Miltner, A. Makaruk, H. Bala and M. Harasek, "Biogas Upgrading for Transportation Purposes; Operational Experience with Austria First Bio-CNG Plant," Vienna University of Technology, Vienna, 2009.

[43] N. Johansson, "Production of liquid biogas, LBG, with Cryogenic and Conventional Upgrading Technology-Description of Systems and Evaluation of Energy Balances," Lunds Universitet, Lunds, 2008.

[44] A. Wellinger, J. Murphy and D. Baxter, The Biogas Handbook: Science, Production & Application, S. Hughes, Ed., Philadelphia: Woodhead Publishing, 2013.

[45] M. J. Tuinier and M. V. S. Annaland, "Biogas Purification Using Cryogenic Packed Bed Technology," *Industrial & Engineering Chemistry Research (I&EC),* pp. 5552-5558, 15 March 2012.