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Compressed Biogas Fuel; An Alternative for Compressed Natural Gas

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Abstract—*Biogas is a renewable source of energy derived from anaerobic digestion of biomass, mainly comprising of dairy waste which is widely available in form of cattle dung in the Indian villages. Its main constituents comprise of CH_4, CO_2, H_2S with traces of nitrogen, water vapours, hydrogen, oxygen, organic silicon compounds and ammonia, their composition depending on the source. In order to obtain methane rich gas, the biogas must pass through two major processes, a cleaning process and an upgrading process. In the later the calorific value and other parameters are adjusted to meet the specifications of vehicle fuel by the removal of CO_2. This upgraded gas can be compressed to Compressed Bio Gas (CBG) which is a very good alternative to the Compressed Natural Gas (CNG) and can be used as a vehicle fuel. The available cleaning and upgrading systems consist of amine scrubbing, pressure swing adsorption, membrane separation, water scrubber, organic physical scrubbing, and cryogenic separation and liquefaction. This paper reviews these technologies and discusses the reasons for the use of Pressure Swing Adsorption at low pressure as the biogas up-gradation technology.*

1. INTRODUCTION

The process of upgradation of biogas generates opportunities for its use as an alternative to a non- renewable fuel namely natural gas. Out of the various biogas upgradation technologies being used today, it is mainly the water scrubbing and pressure swing adsorption that dominated the market, but lately chemical scrubbers, and to a minor extent, membrane separation units, have increased their market share. There are safety and environmental concerns associated with biogas as methane is a green house gas, and also forms explosive mixtures when mixed with air. Therefore, there is a need to reduce the amount of CH_4 emissions into the atmosphere. The downside of the chemical scrubbing is the disposal of used chemical but with the present scientific development, even a zero discharge is possible with almost no methane slip. The available upgrading technologies include Amine scrubbing, Membrane separation, Water scrubbing, Organic physical scrubbing, Pressure swing adsorption, Cryogenic separation and liquefaction. To attain CH_4 rich gas, the biomass undergoes two major processes, a cleaning process in which trace components harmful to the natural gas grid, appliances or end users are removed and an upgrading process, in which the calorific value and other parameters are adjusted in order to meet the specifications of vehicle fuel. Furthermore, if it is to be fed to gas grid as the gas must be odorized beforehand.

2. TECHNICAL ASPECTS OF UPGRADATION TECHNIQUES

The following are the general processes which are generally used throughout the world.

2.1 Amine Scrubbing

Amine scrubbing systems are amongst the most widely used for recovery of CO_2 from breweries, boiler flue gases. Recently amine based purification is gaining popularity in biogas up-gradation systems but is still less popular in comparison to water scrubbing and PSA. In this technology an amine based solvent is used for chemical capture of CO_2 from biogas. Most common amines, which are being used, are blends of Methyl Di-Ethanol Amine (MDEA) and PiperaZine (PZ) often termed activated MDEA [10]

MDEA is most commonly used chemical in industry for removing CO_2 from biogas. In this process an absorber is used to absorb CO_2 and a stripper is used to remove CO_2 from amine solution. Raw biogas is treated with the amine solvent in the absorber. CO_2 in the gas is absorbed almost completely by the solvent and pure CH_4 is let out. Absorption temperature range is between 20-40^{0}C to 45-65^{0}C at inlet of solution [1]. It is an exothermic reaction. From a thermodynamic standpoint low temperatures are favored. Gas at the outlet of the absorber is pure CH_4. Amine is used in stoichiometric excess to avoid any chances of getting CO_2 with CH_4 at the outlet. Pressure in the absorber is kept between 1-2 bar(a) [1]. Rich amine solution is heated by the exit gas stream from the stripper by the use of a heat exchanger. Then this solution is let in the stripper column in which CO_2 rich solution is distributed and passed through a packed column. Here it is contacted with steam and CO_2 is released further down the stripper column. The bottom part of the stripper column is stripped with a reboiler in which heat is added (120^0C-150^0C) [1] and part of the amine solution is boiled, by which CO_2 is removed from solution and steam of removed part then goes into condenser, where condensed liquid again comes into stripper and remaining gases like CO_2 and H_2S are removed. Stripper pressure is slightly higher compared to absorber pressure, usually 1.5-3 bar(a) [1]. There are generally some chances of bacterial growth in amine solution. In order to avoid this some conductor can be used. There are many advantages of this process like it has a retro-fit to existing and new conventional plants, bypass and pure CO_2 stream for storage, and is one of the most developed CO_2 capture options [2]. Inspite of the advantages of the process, it faces challenges like high energy penalty (10%), high capital cost and operating cost, footprint, scaleup, corrosion and degradation (SO_2, O_2 particulate), disposal of lean chemical and high heat requirements.

2.2 Membrane Separation

The principle of membrane separation is that some components of the raw gas are transported through a thin membrane while others are retained. The permeability is a direct function of the chemical solubility of the target component in the membrane. Solid membranes can be constructed as hollow fibre modules, which give a large membrane separation constitutes a conflict between high CH_4 purity in the upgraded gas and high CH_4 yield. The purity of the upgraded gas can be improved by increasing the size or number of the membrane modules, but a larger amount of the CH_4 will permeate through the membranes and is therefore lost. Raw biogas is cleaned before entering in compressor and the membrane to avoid the condensation in the compressor. Water is separated by cooling or condensation and H_2S is removed because it cannot be removed by membranes. H_2S can be separated by activated carbon before compression process. For more precaution an additional filter is provided before compression and membrane separation.

After this cleaning process biogas undergoes compression wherein the pressure is increased. For compression process oil lubricated compressor are used and this oil is to be removed not only to reuse it but also to remove oil content in biogas itself because this oil affects the membrane and reduces its life. The application of this technology is useful when the CH_4 content of upgraded biogas stream (95-99 vol%) [7] is suitable for further utilization, plant capacity is small or medium, biomethane can further be directly utilized or further compressed for bottling purpose. To increase the membrane life additional chemicals and other consumables have to be avoided. Higher flexibility towards process layout and adaption to the local biogas production facility as well as flexible partial load behaviour and plant subtleties are preferred and avoidance of dead time for a fast start-up from cold standby and start/stop operation still needs to be optimized.

2.3 Water Scrubber

Water scrubber works on the principle that CO_2 has much more solubility than CH_4 in water at a particular temperature, pressure and mole fraction. In a water scrubber unit CO_2 is separated from raw biogas and dissolved into water in an absorption column by using high pressure (normally at 6-10 bar(a)) [1]. The CO_2 is then released from the water again in desorption column, by addition of air at atmospheric pressure. There are two columns used in water scrubber, an absorption and desorption column. In adsorption column CO_2 is absorbed by water and in desorption column by the help of air addition at atmosphere pressure the CO_2 is released from water. The operational challenge may include level control, flashing, methane slip etc.

In last decade, a single pass unit without circulation of the water was built [5]. Some of them still exist today, but most new plants have a recirculating system for the water.

When the biogas comes inside the biogas upgrading plant its temperature is around 40^0C [1]. Most of the water is separated and condenses from biogas by increasing the pressure and reducing the temperature before it enters in absorption unit. Counter flow current is maintained of gas and water flows in column to reduce energy consumption as well as losses of CH_4. Equilibrium is maintained between highest partial pressure of CO_2 and lowest partial pressure of CH_4 with water. This results in higher solubility of CO_2 in water and lowest of CH_4. After absorption in water, pressure is reduced about 2.5 bar to 3.5 bar in a flash tower [1] to release remaining CH_4 from water and for its recirculation. Then water is circulated again after removing CO_2 into the desorption column.

The drawback of this method is that the air components O_2 and N_2 are dissolved in the water during regeneration and thus, transported to the upgraded biomethane gas stream. Therefore, biomethane produced with this technology always contains oxygen and nitrogen. As the produced biomethane stream is saturated with water, the final step in upgrading typically consists of a gas drying unit. Corrosion and microbial development on the packings are some of the standard issues.

2.4 Pressure Swings Adsorption

Pressure Swings Adsorption, or PSA is a method for the separation of CO_2 from CH_4 by adsorption/desorption of CO_2 on zeolites or activated carbon at different pressure levels. The adsorption material adsorbs H_2S irreversibly and is thus poisoned by H_2S. So H_2S removing step is often included in PSA process.

The upgrading system consists of adsorber vessels filled with adsorption material. Using normal operation each adsorber operates in an alternating cycle of adsorption, regeneration and pressure build-up. During the adsoprtion phase biogas moves from the bottom into one of the adsorbers. When passing the adsorbers vessel, CO_2, O_2 and N_2 are adsorbed on the adsorbent material surface. The gas leaving top of the adsorber vessel can contains upto 98% CH_4. [3]

The adsorbent material is completely saturated with the adsorbed feed gas components, the adsorption phase is stopped and another adsorber vessel has been regenerated is switched into adsorption mode to achieve continuous operation. Regeneration of the saturated adsorbent material is performed by a stepwise depressurization of the adsorber vessel to atmospheric pressure and finally to near vacuum conditions. Initially the pressure is reduced by a pressure balance with a regenerated adsorber vessel. This is followed by a second depressurization step to almost atmospheric pressure. The gas leaving the vessel during this step contains significant amounts of CH_4 and is recycled to the gas inlet. Before the adsorption phase starts again, the adsorber vessel is re-pressurized stepwise to the final adsorption pressure. After a pressure balance with an adsorber that has been in adsorption mode before, the final pressure build-up is achieved with feed gas.

Recent technology developed in the PSA is L-PSA i.e Low-Pressure swing adsorption, where the feed pressure does not exceed 0.8 kg/cm^{2}g. The advantages of using L-PSA include rotary blowers are used in L-PSA which is more reliable than reciprocating compressors, less maintenance because of lesser moving parts and lesser pressure, almost no lubrication required, safety concerning pressure, no hassles of approval for low pressure biogas scrubber working 1 bar(g). Further this operation is simple to perform, high instrumentation can be avoided, no steady state condition to be reached switch on and switch off mode. It is most suitable for rural environment, low investment cost, downscaling and upscaling of the plant is easily possible, L-PSA combined with CO_2 recovery guarantees almost no methane slip.

2.5 Organic Physical Scrubbing

This is another type of separation method of carbon dioxide and CH_4 from raw biogas involving organic solvent for the separation. The company name haase Energietechnik GmbH manufactures organic physical scrubbers. Genosorb 1753, an organic solvent is normally used in this type of scrubbers. The data described in this section belongs to this solvent only. In organic physical scrubbing, the CO_2 is absorbed in an organic solvent. Genosorb plant is a mixer of dimethyl ethers of polyethylene glycol. It is somewhat similar to the water scrubber. The absorption of CO_2 and CH4 into an organic solvent is described by Henry's law, which states the relation between the partial pressure of a gas and the concentration of the gas in a liquid in contact with the gas [1,10]. CO_2 is highly soluble in organic solvent than in water. Hence the value of Henry's constant for CO_2 is higher. Carbon dioxide has solubility of 0.18 M/atm in selexol [1,10], which is about five times higher than in water. Comparing to CH_4, CO_2 is 17 times more soluble in the Genosorb [1,10]. It is a smaller difference compared to water, in which carbon dioxide is 26 times more soluble than CH_4.

The process is designed in a similar way as a water scrubber with the two main differences that the diameter of the columns is made smaller for lower flow of the organic solvent, and the organic solvent has to be heated before desorption and cooled before absorption.

The biogas is compressed to 7-8 bars [1] and after that it is cooled before injecting underneath of absorption column. Before injecting into the column, the organic solvent is cooled to keep the absorption column around 20^0 C [1]. The temperature will always effect the Henry's constant. So, it is essential to maintain the temperature throughout. For better mass transfer random packing is used inside the column. The CO_2 is absorbed in the organic solvent and the upgraded biogas is dried before it is delivered to the compressor or gas grid or fuelling station.

The organic solvent that leaves the bottom of the absorption column exchanges heat with the organic solvent that is injected to the top of the column. Thereafter, the organic solvent is injected into the flash column, where sudden fall in pressure occurs. The main part of the dissolved CHV and as well as some CO_2 is released and circulated back to the compressor. The exact pressure used in the flash column depends upon the required CH_4 slip, pressure in the absorption column and concentration of CH_4 in the raw biogas. For the regeneration the organic solvent is heated about 40^0C [1] before entering the desorption column. The organic solvent is injected into the top of the column. The pressure is decreased to 1 bar. The heat which is generated by the compressor and regenerative thermal oxidation (RTO) unit is used in the process. It oxidizes the CH_4 slip from the exhaust air. As organic solvent is anticorrosive in nature, the pipe is not made up of stainless steel. Low freezing point of organic solvent helps the system to run at the temperature of -20^0C [1] without any external means.

For upgrading the raw biogas there is a need to remove H_2S. This helps in prevention of system components and also fulfils the requirements of air pollution control regulations. The activated carbons filter is introduced after the amount of water in raw biogas is removed. The water is removed by condensate process and also by increasing the pressure. All trace gases and impurities like ammonia and siloxanes, if exist, could be removed from the raw biogas before upgrading process starts. The manufactures of modern organic physical scrubber assure that the CH_4 recovery is above 98.5 % by using this type of separation process. According to survey, CH_4 content of 98% [7] in upgraded biogas is reached to the some plants. These values may differ depending upon the quality of raw biogas.

Heat integration is still a challenge and the monopoly of proprietary chemical is still an open question.

2.6 Cryogenic separation and liquefaction

Cryogenic separation process is considered for the removal of trace contaminants, mainly in the landfill gas context, removal of main components such as CO_2, N_2 etc. (gas upgrading) and condensation of upgraded biomethane to bio- LNG (LBG).

Cryogenic separation of biogas is based on the fact that CO_2, H_2S and all other biogas contaminants liquefy at different temperature-pressure domains, which make it easy to separate them from CH_4. However, this separation process operates at low temperatures near - 50 ^{0} C [11], and at high pressures, almost 40 bars [11]. These operating requirements are maintained by using a linear series of compressors and heat changers in the process [1].

In cryogenic process low temperature requirement is high for upgradation process to achieve this two cooling options are available; first is direct cooling and other is indirect cooling. In indirect cooling heat exchanger is used a liquid nitrogen is used as cooling agent. This type of method is used in small plants, for big plants this is not advisable because running cost would be very high. In direct cooling process many options are available but mainly compressor, heat exchanger and expansion devises are used in cooling cycle. So for better output combination of direct cooling and indirect cooling is used in biogas up gradation process.

In upgradation of biogas the crude biogas stream passes through the first heat exchanger, which cools the gas down to – 70^{0}C. This heat exchanger makes use of the product stream as cooling medium, which has the advantage of preheating the upgraded biogas before leaving the plant, as well as the energy efficient benefit of the process. The first cooling step is followed by a cascade of compressor and heat exchangers which cool the inlet gas down to -10^{0}C and compress it up to 40 bars [1, 11] before the gas enters into the distillation column. Finally, the distillation column separates CH_4 from the other contaminants, mainly H_2S and CO_2.

By this process CO_2 can be removed from raw biogas, since its condensation temperature is higher than CH_4, it condensate from raw biogas and other impurities like H_2S, water, siloxanes and halogens Because of the high concentration solid carbon dioxide can be a problem in the process by plugging pipes and devices such as heat exchangers.

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The main advantage of cryogenic separation is both the large quantities as well as the high purity of the upgraded biogas. The yield of this separation is 99% for CH_4. Cryogenic approaches have various potential or expected benefits that include hope for low energy demand during upgrading, no contact between gas and chemicals, production of pure CO_2 as side product, possibility to produce LBG and possibility to remove nitrogen from the gas stream.

The main disadvantage of cryogenic separation are that cryogenics processes require the use of much process equipment, mainly compressors, turbines and heat exchangers. The need for the equipment causes this separation technique to be a process with large capital costs. The final price of upgraded biogas using this technique is expensive. There are many operational difficulties pertaining to this method, which still needs to be properly addressed.

3. REASON FOR SELECTION OF BIOGAS UP-GRADATION TECHNOLOGY

The available cleaning and upgrading systems along with the various compressors available, there are some points, which lead to conclude that L-PSA i.e. Low pressure Swing Adsorption at low pressure, followed by CO_2 removal from liquefaction is preferred.

3.1 Required space

The plants facing space constraints which have to perform CO_2 removal, storage of biogas, storage of cascades, doesn't allow for much flexibility on choosing the technology. According to the space optimization study, it was seen that L-PSA needs the least space. It provides a suitable space allowance for installation, operation and maintenance of the plant.

3.2 Technology

Study of the different available technologies from Techno-commercial point of view, PSA uses proven technology with no proprietary or patented items. PSA has got a long track record in biogas up gradation. Besides, lowering the pressure it further boosts the safety issues and lowers the CH_4 slip. It even offers the possibility of CO_2 co-removal in an economical way. LPSA is concluded to be a low cost and is simple to operate. By adopting LPSA technology raw gas can easily be cleaned from moisture as well. In almost all other technologies an additional drier is needed but L-PSA consists of drying media in the column itself. The vented CO_2 can also be recovered by means of purification and liquefaction the CBG production. The gas is first, treated with a hydrogen-sulphide removal system to eliminate the pollutant. H_2S in the gas is absorbed in water and is neutralized by means of an alkali based solvent. The resultant gas is saturated with moisture. Moisture is first removed by flash separation. Before the final drying the gas is compressed, moisture is removed in the compressor itself in two stages in the inter-cooler. A gas cooler further removes moisture through condensation. The drying is completed in a twin molecular sieve based drying system. Before liquefaction the gas should be passed through an activated carbon filter to remove any and all entailing impurities. CO_2 is then liquefied and taken through a specialized separation process where CH_4 is separated. The process consists of boiling and stripping the CO_2 of the remaining. 99.9% pure liquid CO_2 is stored in an insulated tank system. The carbon dioxide can be filled in cylinders by means of cylinder filling station or in a mobile storage link. The separated CH_4 also contains CO_2 and is fed to back to the PSA system ensuring almost no CH_4 slip. Cryogenic has still got the operational problem as CO_2 will sublime under simple cooling condition.

3.3 Sustainability

Attributing to the low pressure, L-PSA has got the lowest demand of energy, whereas organic physical scrubbing has got the maximum demand of energy. L-PSA provides the flexibility to utilize the biogas even directly in future to nearby areas. It is also a dry process and doesn't require and process water except that for cooling purpose. The heating demand is there is Organic physical scrubbing, Amine scrubbing and Water scrubbing, PSA, L-PSA and membrane don't require any process heat. Considering water and energy as the vital aspects of sustainability, L-PSA can be used as an optimal technology

3.4 Startup time

Start-up time is the time, which is required to get a steady state process. In water scrubbing, low temperature needs to be achieved, whereas Amine, Organic and physical scrubbing consist of heating source. Only PSA, L-PSA and Membrane could be considered as on/off process.

3.5 Instrumentation and manpower

A proper instrumentation is required in all the process. Water scrubbing needs to maintain a proper level, flashing pressure, whereas Amine needs to be heated properly to be reused, Cryogenics to totally dependent on the instrumentation as temperature is a crucial parameters. Likewise, organic physical scrubbing and membrane are also highly dependent on proper instrumentation. PSA has got advantage in this manner. Instrumentation can be compromised in this case as the switch over time is an important parameter to govern the quality, which can be adjusted during test run only. L-PSA further adds the benefit of even lowering the instruments.

Manpower and instrumentation are normally inversely proportional to each other. Nevertheless, a basic manpower requirement does play an important role in all the technologies. The more the utility requirement, the more the maintenance, which requires more manpower. Water scrubbing is supposed to be the most manpower intensive process, even after the proper instrumentation followed by Amine, membrane and Organic physical scrubbing. PSA and L-PSA in this manner gives a great deal of flexibility as once running, it doesn't need any such attention.

3.6 Consumables

Water scrubbing needs antifouling agents. The process is followed by the drying step, which may additionally need the drying agent. Organic physical scrubbing needs the non-hazardous organic solvent on regular basis. Amine scrubbing uses Amine solution, which is considered to be hazardous and corrosive. A proper disposal of lean Amine solution has to be planned out in every case. PSA normally uses non-hazardous activated carbon, which can be disposed easily or can be used for other purposes. Membrane doesn't require any specific consumables expect that in H2S removal step. Similar to PSA, non-hazardous Zeolite Molecular Sieve is needed in L-PSA.

3.7 Methane slip

Methane slip is one of the important points in all the technology. Only Amine scrubbing promises close to zero methane slip. L-PSA followed by the CO_2 capturing system also proves the near zero methane slip.

3.8 Miscellaneous

A lot of other parameters like simplicity, widely spread technology, futuristic scenario etc. also indicate that L-PSA is an optimal technique for upgradation of biogas and CO_2 capture.

4. COMPRESSED BIOGAS

After upgradation of biogas, the gas goes to a filling unit via high pressure compressor. CBG is filled into 200 bars in cascades at the filling unit [9]. As a matter of fact, the biogas-bottling plants are one of the most potent tools for mitigating climatic change by preventing carbon emissions from biomass chulha since biogas is used as a cooking fuel and CH_4 emissions from untreated cattle dung and biomass wastes are also avoided.

The clean and upgraded biogas can be introduced into the natural gas grid since it is comprised of mostly CH_4, the same main component as natural gas. The purified biogas can be bottled in CNG cylinders to obtain CBG and compressed biogas (CBG) can be used as an alternative to CNG. The main application of CBG can be as a vehicle fuel.

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