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STUDY OF BIOGAS PURIFICATION AND STORAGE TECHNIQUES- A REVIEW

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***Abstract*- In this review paper,study of different methods of scrubbing of CO2 and H2S and the techniques of storage were carried out . Water scrubbing method was studied in detail to understand the scrubbing efficiency at different pressures and retention time of gas in water. Scrubbing efficiency and the economics of the process were studied to obtain a feasible user friendly method of purification of biogas**.

***Keywords* – Biogas compression, gas storage, gas purification, methods, solubility, efficiency.**

1. INTRODUCTION

Biogas is produced in many different environments including landfills, sewage sludges and during anaerobic degradation of organic materials.Biogas is comprised of methane(CH4)-40-75%, CO2-25 to 55% by volume and other compounds including hydrogen sulphide, water vapour and traces of some gases. The functional entity of biogas is **METHANE** (CH4) and rests are nonentity mainly Cardon dioxide and Hydroden sulphide, which makes the purification process of biogas mandatory for its use.

Main drawback of CO2, H2S and water vapour is they reduce the Calorific value and make it uneconomical to compress and transport to longer distances. It istherefore necessary to remove these gases before compression[1].

It is not possible to liquified Methane at ambient temperature (Critical temperature- -82.5^{O}C) and pressure (critical pressure – 47.5 bar) conditions.[1]

Storage requirements andconcentrate energy content are increased by compression of biogas and the resulting increases in pressure helps overcoming resistance to gas flow. Compression is better in the scrubbed biogas.

TABLE 1
MOST COMMONLY USED BIOGAS SYSTEM [2]

Pressure	Storage device	Materials
Low (0.138-0.414 bar)	Water sealed gas holder	Steel
Low	Gas bag	Rubber,Plastic,Vinyl
Medium (1.05-1.97 bar)	Propane or Butane tanks	Steel
High (200 bar)	Commercial gas cylinder	Alloys

Biogas is about 20% lighter than air and has an ignition temperature in the range of 650 to 750 degrees C. (1,200-1,380 degrees F.). It is an odorless and colorless gas that burns with a clear blue flame similar to that of natural gas. However, biogas has a calorific value of 20-26 MJ/m3 (537-700 Btu/ft3) compared to commercial quality natural gas' caloric value of 39 MJ/m3 (1,028 Btu/ft3)[3]

2. METHODS OF PURIFICATION

The biogas scrubbing system consists of three units, the hydrogen sulphide (H2S) removing unit, Carbon dioxide (CO2) removing unit, and moisture trapping unit. [5] The presence of incombustible gases like CO2, H2S and water vapour reduce its calorific value and make it uneconomical to compress and transport tolonger distances. It is therefore necessary to remove these gases before compression.[1]
The process of purification of Biogas consists of separation of CO2, H2S and water vapour.

2.1METHODS OF CO2 SCRUBBING

- Water scrubbing
- Chemical absorption
- Adsorption on a solid surface
- Membrane separation

- Cryogenic separation
- Chemical scrubbing with amines [6]
- Chemical scrubbing with glycol[6]

2.2METHODS OF H2S SCRUBBING

- Dry oxidation process
- Adsorption using Iron oxide
- Liquid phase oxidation process
- Lime scrubbing
- Air injected into the digester biogas holder[6]
- Iron chloride added to the digester [6].

2.3METHODS OF WATER VAPOUR REMOVAL

- Physical Drying Method[7]
- Chemical Drying Method[7]

3. SCRUBBING OF CO2:

As Carbon dioxide has a higher solubility in water than methane. Carbon dioxide will therefore be dissolved to a higher extent than methane, particularly at lower temperatures.

3.1 WATER SCRUBBING

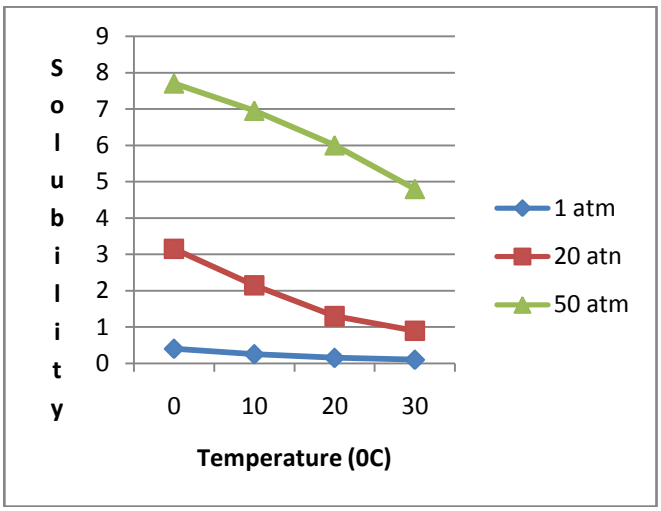
Water scrubbing is used to remove CO2 and H2S from biogas, since these gases are more soluble in water than methane. Water scrubbing can also be used for selective removal of H2S since it is more soluble than CO2 in water.

TABLE 2
APPROXIMATE SOLUBILITY OF CO2 IN WATER [8].

Pressure (atm)	Solubility in kg of CO2 per kg of water at different temperatures			
	0	10	20	30
1	.40	0.25	0.15	0.10
20	3.15	2.15	1.30	0.90
50	7.70	6.95	6.00	4.80

The basis of this process is high pressure scrubbing of the biogas with pressurised water this removes a significant of the acid gas contaminants including CO2 and H2S which can be released from the wash water in air or stream stripping tower. The resulting regenerated water can be recirculate for further use or just used on time

Graph 1 Approximate solubility of CO2 in water



3.2 CRYOGENIC SEPARATION

This method is based on the fact that CO2 contaminant can be separated form methane from the fact that each contaminant liquefies at different temperature and pressure domain and this process operate at temperature around -100^0Cand high pressure almost 40 bar. The main advantage of cryogenic separation is the high purity of the upgraded biogas(99% methane) as well as the large quantity that can be efficiently processed. The main disadvantage of this method is that cryogenic process require costly equipment mainly compressors, turbine and heat exchanger and so the overall cost of plant increases.

3.3 CHEMICAL ABSORPTION

Chemical absorption is capable of producing gas of high methane content above 95% and has no methane losses; hence it is widely used on large scale applications. It was found that when sodium hydroxide was used for scrubbing CO2 at different concentration level, it was observed that with increase in concentration level (1M, 2M, 3M) there was an increase in absorption rate and thus the methane production. The highest removal efficiency was recorded to be 66%. [9]

4. SCRUBBING OF H2S

The presence of H2S in biogas leads to corrosion of internal combustion engine. Most of the technologies for the removal of H2S content are

chemically based and expensive to operate, thereby reducing the economic value of Biogas.

4.1. WATER SCRUBBING OF H2S

The easiest method of biogas purification is water scrubbing which uses of the characteristics of hydrogen sulphide solubility in water. Different water levels in biogas flow rate were maintained to remove hydrogen sulphide content from biogas

TABLE 3

THE REMOVAL EFFICIENCY OF H2S FROM BIOGAS FOR DIFFERENT WATER LEVEL WITH BIOGAS FLOW RATE 140 *L*/MIN AFTER WATER SCRUBBING FOR 30 SEC. [10]

Water scrubbing time (sec)			30
Water level(cm)	50	60	70
Trail	3	3	3
Concentration of H2S(ppm)	4000.0	3633.3	2933.3
The removal efficiency*(%)	33.3±7.6	39.4±14.3	51.1±9.8

*Without circulating water system.

TABLE 4
THE REMOVAL EFFICIENCY OF H2S FROM BIOGAS FOR DIFFERENT WATER LEVEL WITH BIOGAS FLOW RATE 140 L/MIN AFTER WATER SCRUBBING FOR 90 SEC.[10]

Water scrubbing time (sec)			30
Water level(cm)	50	60	70
Trail	3	3	3
Concentration of H2S(ppm)	4000.0	3633.3	2933.3
The removal efficiency*(%)	33.3±7.6	39.4±14.3	51.1±9.8

*Without circulating water system.

4.2 THE OXIDATION PROCESS:

Removal of sulphur from biogas involves oxidizing hydrogen sulfide with atmospheric oxygen. A small amount of air (3-6% volume of produced biogas) can be introduced directly into a bio-reactor filled with digested matter. This can be done by pumps that supply suitable amounts of air. Chemical reaction for this oxidation process can be stated as shown below: 2H2S+ O2 _2S + 2H2O.[11]

4.3 LIME PROCESS:

Desulphurization of biogas using solid quick lime or liquid slaked lime is very old and familiar process and yet has not been used on a large scale. To handle dissolved or suspended slaked lime in large quantity, specially designed equipment is required. If biogas contains more CO2, removal of H2S up to satisfactory level becomes more difficult. The CO2 quickly reacts with quick and slaked lime. During the process Ca(HCO3)2 is formed which may react with Ca(SH)2 .This may produce H2S again. If quick lime is available, this process can be used for desulphurization.[11]

4.4 ADSORPTION ON ACTIVATED CARBON:

Hydrogen sulphide is adsorbed on the inner surfaces of engineered activated carbon with defined pore sizes. Addition of oxygen (in the presence of water) oxidizes H2S to plane sulphur that binds to the surface. In order to increase the speed of the reaction and the total load, the activated carbon is either impregnated or doped (by addition of a reactive species before formation of the activated carbon) with permanganate or potassium iodide (KI), potassium carbonate (K2CO3) or zinc oxide (ZnO) as catalysers.[12]

4.5BIOLOGICAL H2S REDUCTION:

Biological desulphurisation uses naturally occurring aerobicbacteria present in air, to breakdown the H2S. The air isinjected in small quantities into the biogas in the head space ofthe digester. Because there are no chemicals involved, thereare no operational costs & it is environmentally friendly. If theretention time of the biogas in the digester is greater than 1 –1.5 hrs, we can expect a reduction of H2S up to 95%.[13]

5. CONCLUSION:

Amongst various method of removal of CO2 ,Cryogenic method gives 99% removal efficiency . However the costly equipments

likecompressor ,turbine etc are used and hence this method becomes uneconomical .In chemical adsorption method CO2 removal efficiency is near about 66% and its efficiency increases as concentration level of solution .Water scrubbing is best method among all the methods. In this the solubility of CO2 in water increases as the pressure increases . The scrubber was designed for 95 % CO2 absorption from rawbiogas in pressurized water for 2 m3/h inlet gas flow rate at 6 bargas pressure.

H2Sscrubbing is done by many methods but most user friendly method is water scrubbing, in this method there are two parameters which affect the h2s concentration mass flow rate and time for scrubbing .As the height of water column increases the h2s concentration level decreases whereas the time for scrubbing increases the efficiency of removal ofH2S concentration is lower as compared to shorter time period.

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