A Review on Best Suitable Method for Biogas Purification

S. C. Labde¹, S. D. Kore², R. L. Patil³, S. N. Patil⁴, S. M. Mulye⁵

^{1, 2, 3, 4, 5} Sinhgad Institute of Technology, Lonavala, Maharashtra-410401, India

Abstract- The biogas derived from the biomass is commercially used as fuel. But it is impure as it contains 30-45% of CO₂, 0.005-2% of H₂S, traces of water vapour and remaining methane which is only the combustible component in the biogas. As CO₂ reduces the volumetric efficiency and H₂S corrodes the metallic part therefore impure biogas does not acts as a good fuel for the domestic as well as industrial applications. Hence purification of biogas is necessary before use it as a fuel. Different methods for biogas cleaning and upgrading are used and they differ in functioning as well as necessary quality conditions of the gas. This review discusses the impact of impure biogas and its purification techniques.

Keywords- methane, CO_2 , H_2S , chemical adsorption, water scrubber, membrane etc.

I. INTRODUCTION

The International Energy Agency projects that the world's electrical generating capacity will increase to nearly 5.8 million megawatts by the year 2020, up from about 3.3 million in 2000. However, the world supplies of fossil fuelsour current main source of electricity-will start to run out from the years 2020 to 2060, according to the petroleum industry's best analysts. Shell International predicts that renewable energy will supply 60% of the world's energy by 2060. The World Bank estimates that the global market for solar electricity will reach \$4 trillion in about 30 years. Other fuels such as Hydrogen and biomass fuels could help replace gasoline. It is estimated that the United States could produce 190 billion gallons per year of ethanol using available biomass resources in the USA. And unlike fossil fuels, renewable energy sources are sustainable. They will never run out. According to the World Commission on Environment and Development, sustainability is the concept of meeting "the needs of the present without compromising the ability of future generations to meet their own needs." That means our actions today to use renewable energy technologies will not only benefit us now, but will benefit many generations to come.

Renewable energy deriving from biomass sources has great potential for growth to meet our future energy demands [4]. Biogas is a very important source of renewable methane. It is produced from anaerobic biodegradation of biomass in the absence of oxygen and the presence of anaerobic microorganisms ^[4]. Bio methane production and its use have experienced a great development in recent years. European market of the bio methane production is essentially developed in German where the first plants were started in 2007 and there were more efforts for regulatory the technical standard for its grid injection, furthermore other countries, as Austria, Switzerland, Sweden and the Netherland, have developed several plants for bio methane production ^[12]. Bio methane is derived from biogas which is obtained from the organic waste and commonly it is known as biogas.

Biogas is a promising renewable resource which can help to reduce environment pollution and relieve the energy crisis. Its market demand is rising globally ^[1]. The purification of biogas is one of the key technologies in its application because its purity weighs heavily against its quality. Biogas is a valuable renewable energy that usually contains 60-65% CH₄ (methane), 35-40% CO₂ (carbon dioxide), and other trace amounts of components such as 5-10% H₂O (water), 0 -1% O₂ (oxygen), and 0.005 -2% H₂S (hydrogen sulphide) by volume of biogas ^[17].

1.1 Impurities

1. CO₂

Biogas contains 30-40% of CO_2 which is noncombustible component. It has low calorific value. Due to which performance of working application will affected. Also emissions are increased after combustion of biogas. Therefore removal of CO_2 from biogas is necessary before combustion [17].

2. H₂S

0.005-2% of H_2S is present in biogas. It may because corrosion in gas storage tanks and engines. Toxic concentrations of H_2S remain in biogas. SO_2 and SO_3 are formed due to combustion which is more toxic than H_2S and also cause corrosion with water ^[6].

3. WATER

Percentage of water in biogas is up to 5-10%. Because of water, efficiency of biogas decreases. Corrosion in compressors, gas storage tanks and in engines takes place due to reaction with H_2S , NH_3 and CO_2 to form acids. Water accumulates in transmission pipes and leads to corrosion of pipes. Due to high pressure condensation and freezing occurs in the biogas plant ^{[6].}

4. SILOXANE

Siloxane has low toxicity, biodegradability, high thermal stability, low surface tension. Percentage of siloxane in biogas is very less that's why it doesn't affect more on the performance of any operation done by biogas ^[6].

5. DUST

Minor amount of dust is present in biogas. Dust is of coarse and fine size. Deposition of dust in compressor leads to clogging of gas storage tanks.

II. LITERATURE REVIEW

Now a day's use of non con-conventional energy sources is increased in various areas. Unpurified biogas decreases efficiency of the system. Different methods for biogas cleaning and upgrading are used. They differ in functioning, the necessity quality conditions of the incoming gas, the efficiency and operational procedures. For the purification two major steps are performed:1) a cleaning process to remove impurities and 2) an upgrading method to adjust the calorific value. CO₂ and H₂S are the most obtained impurities in biogas ^[6].There are many methods used for the purification of biogas. In those methods some method separates CO₂ or H₂S and some methods separate both.

Basic mechanisms are used for separation of CO_2 and H_2S from biogas like physical and chemical absorption, adsorption on solid surface, membrane separation, cryogenic separation and chemical conversion etc. when the scrubbing method is used for separation of CO_2 , obtained gas becomes equal to natural gas.

2.1 CO₂ SEPARATION METHODS

Multistage membrane reactors were used for the removal of CO_2 from biogas. This method is carried out by two stages. In first stage reactor, CO_2 is absorbed 95% and in second stage reactor $Ca(OH)_2$ is completely absorbed. Using the reaction in between CO_2 and $Ca(OH)_2$ purification of biogas is done. Reactor was run for at least 5 hrs continuously ^[1]. Gas-liquid membrane contractor performed an experiment on CO_2 separation from biogas using membrane contactor. For separation, absorption technique is used. By this method it is

observed that CO_2 absorption increases with increase in solvent concentration. Potassium-argrininate (PA) has higher affinity towards CO_2 and biogas is upgraded by 99.15% by vol. for 0.69 to 0.78 mol/mol of PA^[2].

An expanded granular sludge bed system is used for removal of CO_2 by using municipal solid waste (MSW). Combined CaCO₃ precipate is formed i.e. carbonation process takes place. After the process of carbonation 87.1-91.4% of pure methane is obtained ^[8]. In scrubbing with water technique pumped water is sprayed by nozzles from the top side of the liquid column. Unpurified biogas gas is passed from bottom of the column. Due to low density gas flows upwards and during this stage CO_2 present in the biogas gets soluble in water. Amount of CO_2 absorbed is calculated as the concentration of CO_2 from the outlet water. After carbonation methane content increased to 87.1-91.4% ^[14].

In amine absorption process monoethanolamine (MEA) and diethanolamine (DEA) were used to absorb the CO_2 from natural gas. Another process is removal of CO_2 by using membranes based on gas separation components ^[15].

2.2 H₂S SEPARATION METHODS

Chemical-biological process carried out elimination of H_2S by using Acidithiobacillus ferroxidans CP9. After chemical absorption of H_2S , the concentration of H_2S is reduced. Removal efficiency of 98% was achieved. If glucose is added in the ferroxidant then purification efficiency increases^[3].Microaerobic treatments for biogas desulfurization like full scale anaerobic reactors treating sewage sludge was tested. If concentrated oxygen produced from air is used then it is best suitable alternative for ferric salt^[7].

Regenerable TiO₂/zeolite composite where zeolite is absorbent and TiO₂ as a photo catalyst was used for the separation of H_2S . Simultaneous removal of H_2S and CO₂ takes place on surface of cheap neutral zeolite with an ultrasonic calcination way. It was observed that 5-TiO₂ zeolite gives better purification due to desulfurization^[10].

Three towers were used for absorption of organic compounds. Nitrogen sulphuric acid and volatile organic compounds are absorbed by H_2SO_4 , NaOH and NaClO solution respectively. After passing through three cylinders H_2S is absorbed and approximately reduced to zero ^[17].

In direct selective oxidation to sulphur by V_2O_5 -CeO₂ structured catalyst method, removal of H₂S from biogas at 150°C-200°C was investigated. The wash coat coating quality was evaluated with adhesion test and SEM analysis. The effect

on the catalytic performances of the vanadium loading variable between 2 wt% and 19 wt% was evaluated $^{[13]}$.

2.3 COMBINED CO₂ AND H₂S REMOVAL METHODS

In packed column reactor CO_2 and H_2S absorption technique is used. NaOH, $Ca(OH)_2$ and MEA solutions were used as absorbent. These solutions are circulated through column opposite to flow of the biogas. Results of this process revealed that aqueous solutions were effective for removal of CO_2 and H_2S which gives 90% removal efficiency ^[4]. An experiment using mono ethanolamine (MEA) solution in packed bed, with the tower of total height 370cm and 25cm diameter consist 3 beds of 60cm height were carried out. CO_2 and H_2S mixture compressed at required pressure and passed through bottom side of tower. After selective absorption Testo-350 gas analyser is used; this shows how much amount of gas is absorbed. Changes in amine concentration alter the absorption rate ^[18].

In an industrial by product as sorbent, basic oxygen furnace (BOF) slag with glucose solution is used.CO₂ and H₂S gas mixture was sent to reactor for 5 min at flow rate of 10L/min. when BOF slag is introduced in a reactor CO₂ and H₂S removal takes place. Optimal range of CO₂ removal was observed for L/S ratio between 0.05 and 0.2 L/kg. For simultaneous removal of H₂S and CO₂ required L/S ratio was 0.2 L/kg^[9]. Polymer membrane peek hollow fibre of Porogen Corporation is used in a cartridge of 155x1210mm dimensions. Test was carried out by varying inlet pressure, feed flow rate and permeate pressure of the biogas to evaluate effect of this parameter on purity and recovery of methane. Results are obtained by comparing the inlet and outlet contain of CO₂ and H₂S^[12].

Hollow fibre membrane contactors absorption technique is used for separation of CO2 and H2S from methane. Two types of commercial hollow fibers were used i.e. PTFE and PFA. For selective removal of acid gases from pressurized steam distilled water, aqueous sodium hydroxide and amine solution of different concentration were tested. Due to the smaller dimensions and higher porosity and higher liquid mass transfer coefficient PTFE and PFA are more superior than other fibres ^[16]. Three microalgal strains were used with varies mixed light-emitting diode light wavelengths upgradation of biogas. The three strains are for chlorellavulgaris, scenedesmus oblquus and neochloris. Results show that microalgal biomass production gives nutrient reduction, CO₂ removal and biogas enrichment^[5].

Biogas is purified by using anaerobic digestion of sludges in a wastewater treatment plant. In this method along

with scrubbing tower, activated carbon filters are used. The effluent biogas from the scrubbing towers presented an H_2S concentration less than 1 ppm and zero or undetectable values were obtained for up to 58 analysed trace elements^[11].

2.4. SEPARATION OF IMPURITIES

In biogas many other impurities are present like water, siloxanes, halogenated carbon hydrates, dust air, NH_3 etc. These impurities are separated by various absorption methods and cryogenic separation. These impurities are present in very minute proportion. And they does not much affect on the performance of biogas. Hence removal of these impurities are not that much important like H_2S , CO_2 etc ^[6].

III. CONCLUSION

Different methods for the purification of biogas are reviewed. Different techniques available for the purification of biogas such as chemical and physical absorption, chemical adsorption, and cryogenic separation methods are discussed. Some methods separates CO_2 and H_2S independently and some methods separate simultaneously. It is found that water scrubbing method removes CO_2 and H_2S simultaneously and efficiently. In this method when pressure of the inlet biogas is increased, absorption of CO_2 and H_2S in water increases. As water is used as absorbent it is economical method and can be used in a cyclic process.

REFERENCES

- Haoran Y., Tao Z., Xi L., Jun Z., Yabing Z., Xiaoning L., Yilu C., Xiaoyu Y., Shuya W., "Continuous process of biogas purification and co-production of nano calcium carbonate in multistage membrane reactors", Chemical Engineering Journal, 2015, 271, pp. 223–231.
- [2] Shuiping Yan ,Qingyao He , Shuaifei Zhao ,Yuanyuan Wang , Ping Ai, "Biogas upgrading by CO₂ removal with a highly selective natural amino acid salt in gasliquid membrane contactor", Chemical engineering and processing 85 (2014)e125-e135.
- [3] Ching-Ping T.,Kuo-Ling H., Wei-Chih L., Ying-Chien C., Yu-Pei C., "Elimination of high concentration hydrogen sulfide and biogas purification by chemical– biological process", Chemosphere, 2013, 92, pp. 1394-1401.
- [4] Tippayawong N., Thanompongchart P., "Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a

packed column reactor", Energy, 2010, 35, pp. 4531-4535.

- [5] Zhao Y., Sun S., Hu C., Hui Z., Xu J., Ping L., "Performance of three microalgal strains in biogas slurry purification and biogas upgrade in response to mix light-emitting diode light wavelengths", Bioresearch technology, 2015, 187, pp. 338-345.
- [6] Ryckebosch E., Drouillon M., Vervaeren H., "Techniques for transformation of biogas to biomethane", biomass and bioenergy, 2011, 35, pp. 1633-1645.
- [7] Díaz I., Ramos I., Fdz-Polanco M., "Economic analysis of microaerobic removal of H₂S from biogas in fullscale sludge digesters" Bioresource Technology, 2015, 192, pp. 280–286.
- [8] J. Luo, X. Lu, J. Liu, G. Qian, Y. Lu, "Biogas recirculation for simultaneous calcium removal and biogas purification within an expanded granular sludge bed system treating leachate", Bioresource Technology, 2014, 173, pp. 317-327.
- [9] Sarperi L., Surbrenat A., Kerihuel A., Chazarenc F., " The use of an industrial by-product as a sorbent to remove CO₂ and H₂S from biogas", Journal of Environmental Chemical Engineering-2, 2014, 2, pp. 1207–1213.
- [10] Liu C., Zhang R., Wei S., Wang J., Liu Y., Li M., Liu R., "Selective removal of H₂S from biogas using a regenerable hybrid TiO₂/zeolite composite", Fuel, 2015, 157, pp. 183-190.
- [11] Osorio F., Torres J. C., "Biogas purification from anaerobic digestion in a wastewater treatment plant for biofuel production", Renewable Energy, 2009, 34, pp. 2164-2171.
- [12] Iovane P., Nanna F., Ding Y., Bikson B., Molino A., "Experimental test with polymeric membrane for the biogas purification from CO₂ and H₂S", Fuel, 2014, 135, pp. 352-358.
- [13] Palma V., Barba D., "H₂S purification from biogas by direct selective oxidation to sulphur on V_2O_5 -CeO₂ structured catalysts", Fuel, 2014, 135, pp. 99-104.
- [14] Kolaczkowskia S. T., Awdrya S., Led C. D., Nuckolsb M. L., Smithe T., Thomas D., "Removal of CO₂ from a

submersible atmosphere by scrubbing with water— Experiments in a single column", chemical engineering research and design, 100, 2015, pp. 157-169.

- [15] Peters L., Hussain A., Follmann M., Melin T., Hagg M. B., "CO₂ removal from natural gas by employing amine absorption and membrane technology—A technical and economical analysis", Chemical Engineering Journal, 2011, 172, pp. 952-960.
- [16] Marzouk S., Al-Marzouqi M. H., Teramoto M., Abdullatif N., Ismail Z. M., "Simultaneous removal of CO_2 and H_2S from pressurized $CO_2-H_2S-CH_4$ gas mixture using hollow fiber membrane contactors", Separation and Purification Technology, 2012, 86, pp. 88-97.
- [17] V. K.Vijay, S.S. Kapdi, S.K. Rajesh, R. Prasad, "Biogas scrubbing, compression and storage: perspective and prospectus in Indian context", Renewable Energy, 2005, 30, pp. 1195–1202.
- [18] Hamid R.G., DariushM., "Selectivity study of H₂S and CO₂ absorption from gaseous mixtures by MEA in packed beds", chemical engineering research and design, 2008, 86, pp. 401–409.