RECENT REVIEWS ON BIOGAS PURIFICATION TECHNOLOGIES

K. A. Sahu, S. R. Kalbande and V. B. Shinde
Department of Uncoventional Energy Sources and Electrical Engineering.
Dr. Panjabrao Deshmukh Krishi Vidyapeeth Akola

Abstract
The main objective of the research paper is to study the different biogas purification technologies. Biogas is a clean renewable energy source for rural India. It mainly consists of methane (55-70%), carbon dioxide (30-45%), hydrogen sulphide (<1%) and some traces of water vapour. The CO_2, H_2S and moisture degrade the quality of biogas. They corrode the metal parts, also effect the calorific value of biogas in a negative manner. These contaminants also lead to the formation of SO_2 which leads to smog and acid rains. The removal of these contaminants especially H_2S and CO_2 will improve the quality of the biogas for its further uses. Biogas upgrading market is facing challenges in term of operating costs and energy consumption. The selection of appropriate technology for biogas purification depends on the biogas requirements, site, availability of local materials and also low cost materials. The study revealed that the use of various local and low cost materials i.e. iron turnings, limestone etc. will purify the biogas and make it more effective to use.
Keywords: Biogas, CO_2 removal, H_2S removal, Methane.

Introduction

Growing demand of energy and the exhausting of fossil fuel, the research and development of renewable energy has attracted more attention. Biogas generated by the biological degradation of organic compound, has been considered as a valuable energy carrier, and it is now playing a key role in emerging market of renewable energy. Total biogas production in India is 2.07 billion m^3/year.

Biogas is a clean renewable energy source for rural India. It mainly consists of methane (55-70%), carbondioxide (30-45%), hydrogen sulphide (<1%) and some traces of water vapour. In composition of biogas methane, carbon dioxide, hydrogen sulfide, nitrogen, oxygen, ammonia, chlorinated organic matter, silanes, siloxanes, volatile phosphorous substances and other volatile trace compounds are found.

Non-combustible constituent of biogas, carbon dioxide does not contribute to the combustion; in fact it lowers the heating value of biogas and increases the compression and transportation costs. So, there is an immense need of removal of carbon dioxide from biogas. Biogas production and subsequent purification will significantly satisfy the fuel requirement in rural as well as urban transport. For using biogas as vehicle fuel, it has to be purified by removing the impurities like carbon dioxide, hydrogen sulphide and water vapour. These impurities can have detrimental effect on the life cycle and performance of the engine Therefore it is necessary to purify the biogas before using it for combustion. The purified biogas could be a decentralized source of fuel with uninterrupted supply using cheap and locally available resources. It will generate sufficient opportunities for employment too in rural areas.

Biogas is produced by anaerobic digestion of biomass such as cattle dung, vegetable waste, municipal solid waste, poultry droppings, industrial waste water and landfill etc. Main products of the anaerobic digestion are biogas and slurry (Manjula and Mahanta 2017).It promotes a technology for converting waste to energy which greatly supports Clean Development Mechanism (CDM) to help reduce GHGs emissions.

At present biogas is used mainly in cooking and lighting. The gas produced in digester is transported by piping to nearby kitchens on pressure developed in digester. It is possible to improve quality of biogas by removal of CO_2, H_2S and enriching its methane content up to the natural gas level. After methane enrichment and compression it can be used as vehicle fuel like CNG. Any low cost technique to remove carbon dioxide and hydrogen sulfide from biogas can make biogas a techno-commercially viable fuel (Divyang *et al.,* 2015).

Research work carried out by various authors on biogas purification technologies for H_2S removal

Kapdi *et al.,* (2018) studied that Due to rapid industrialisation and urbanisation in last few decades there is a huge pressure on fossil fuels and need for the alternatives. Biogas is one of the most important renewable source which would cope up to cater for heat and power. At present it is not possible to transport biogas over long distances and to put in use to the extent where it is required. Biogas is a clean-burning, renewable fuel that is 60-70% methane and can be used to power household appliances and generate electricity.

Michael *et al.,* (2016) studied that the Hydrogen sulphide is removed by using catalyst iron oxide in the form of oxidised steel wool or iron turning from any workshop. Once biogas comes in contact with this wool, iron oxide is converted into elemental sulphur. The chemical equations are as follows;

$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$

$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S$

Antonio *et al.,* (2014) studied that raw biogas has produced many applications. However, its hydrogen sulfide content must be eliminated to avoid possible damages to equipment and hazards to users and the environment. Among the various set-ups available for removal of hydrogen sulfide from biogas is a fixed-bed of steel wool. This study investigated the effectiveness of iron steel wool in eliminating hydrogen sulfide in a biogas, its efficacy and the amount of H_2S removed. A three-stage removal system was installed for the removal of Hydrogen Sulfide. The raw gas was produced by a continuous flow type Biogas Digester. Testing the steel wool as an adsorbent indicates that it has potential as an effective and economical adsorbent for H_2S removal. Polyvinyl-chloride (PVC) columns were constructed and a biogas mixture passed through the columns containing the steel wool. The most significant results indicate the intake H_2S concentrations averaging 170 ppm – 150 ppm and 0 ppm – 0.1 ppm output, as measured by a portable hydrogen sulfide gas analyzer. Removal efficiencies over 95% were observed for a majority of the run time. Elimination capacities recorded were between 3-4 Standard liters per minute (SLPM). Temperature in the system varied from 26-27°C and the relative humidity in the spent column was above 90%. The removal of Hydrogen Sulfide in a biogas demonstrated good performance throughout the testing phase. Based on the field measurements, the system required only a few days for startup. The desulfurization systems, under normal operating conditions, had reduced 170 ppm of H_2S to 0 ppm with accuracy of ± 0.1ppm.

Fernandez *et al.,* (2017) investigated the option to purify biogas from small-scale biogas plants by entrapping CO_2 and H_2S with regionally available biomass ash. Connected to the existing biogas plant Neustift (Tyrol) wood ash placed in a 1 m3 container was used as a trap for CO_2 and H_2S in the biogas. With the process conditions chosen, for a period of a few hours CO_2 was trapped resulting in pure methane. The removal of H_2S was much longer-lasting (up to 34 d). The cumulative H_2S uptake by the biomass ash ranged from 0.56 to 1.25 kg H_2S per ton of ash. The pH of the ash and the leachability of Lead and Barium were reduced by the flushing with biogas, however toxicity towards plants was increased thus reducing the potential of ash use in agriculture. It can be concluded that biomass ash may be used for removal of hydrogen sulphide from biogas in small and medium biogas plants. The economic evaluation, however, indicated that the application of this system is limited by transport distances for the ash and its potential use afterwards.

Biogas purification technologies for CO_2 removal

Virendra *et al.,* (2014) stated that the raw biogas is first passed through a CO_2 separation unit. Limestone crystals are used to remove carbon dioxide. Limestone reacts with carbon dioxide to form calcium carbonate. The chemical reaction is as follows:

$CaO + CO_2 \rightarrow CaCO_3$

Zhou *et al.,* (2017) studied that Biogas is a renewable fuel source of methane that can be used as energy for vehicles after a purification process to remove impurities (Biogas upgrading and cleaning). However, removal of CO_2 from methane is one of the critical steps for biogas upgrading and is limiting its commercial application. An overview of the materials in technologies of separation (membrane) and sorption (sorbents) know-how, including chemisorbents and physisorbents, has been made with a particular emphasis on biogas upgrading. The alternative properties and possibilities of different technologies and materials for CO_2 separation, including alkanol amine, solid alkanolamine, zeolites, carbonaceous, metal-organic frameworks (MOFs), zeoliticimidazolate frameworks (ZIFs), and membrane applied for purifying raw biogas (upgrading) to produce bio-methane and on the other hand, to reduce CO_2 emission from fossil fuel are discussed.

Tippayawong *et al.,* (2009) found that the Biogas from anaerobic digestion of biological wastes is a renewable energy resource. It has been used to provide heat, shaft power and electricity. Typical biogas contains 50-65% methane (CH_4), 30-45% carbon dioxide (CO_2), moisture and traces of hydrogen sulphide (H_2S). Presence of CO_2 and H_2S in biogas affects engine performance adversely. Reducing CO_2 and H_2S content will significantly improve quality of biogas. In this work, a method for biogas scrubbing and CH_4 enrichment is presented. Chemical absorption of CO_2 and H_2S by aqueous solutions in a packed column was experimentally investigated. The aqueous solutions employed were sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) and mono-ethanolamine (MEA). Liquid solvents were circulated through the column, contacting the biogas in countercurrent flow. Absorption characteristics were examined. Test results revealed that the aqueous solutions used were effective in reacting with CO_2 in biogas (over 90% removal efficiency), creating CH_4enriched fuel. H_2S was removed to below the detection limit. Absorption capability was transient in nature. Saturation was reached in about 50 min for $Ca(OH)_2$, and 100 min for NaOH and MEA, respectively. With regular replacement or regeneration of used solutions, upgraded biogas can be maintained. This technique proved to be promising in upgrading biogas quality.

Mojica *et al.,* (2018) studied the development of a low-cost biogas filtration system for alternating current generator to achieve higher efficiency in terms of power production. A raw biogas energy comprises of 57% combustible element and 43% non-combustible elements containing carbon dioxide (36%), water vapor (5%), hydrogen sulfide (0.5%), nitrogen (1%), oxygen (0 – 2%), and ammonia (0 – 1%). The filtration system composes of six stages: stage 1 is the water scrubber filter intended to remove the carbon dioxide and traces of hydrogen sulfide; stage 2 is the silica gel filter intended to reduce the water vapor; stage 3 is the iron sponge filter intended to remove the remaining hydrogen sulfide; stage 4 is the sodium hydroxide solution filter intended to remove the elemental sulfur formed during the interaction of the hydrogen sulfide and the iron sponge and for further removal of carbon dioxide; stage 5 is the silica gel filter intended to further eliminate the water vapor gained in stage 4; and, stage 6 is the activated carbon filter intended to remove the carbon dioxide. The filtration system was able to lower the non-combustible elements by 72% and thus, increasing the combustible element by 54.38%. The unfiltered biogas is capable of generating 16.3 kW while the filtered biogas is capable of generating 18.6 kW. The increased in methane concentration resulted to 14.11% increase in the power output. The outcome resulted to better engine performance in the generation of electricity.

Orhorhoro *et al.,*(2016) studied the biogas purification which is the removal of impurities so as to improve the efficiency of gas produced, ensure the safety of end users and prolong the life of the equipment cannot be neglected. This paper is focused on the design and performance evaluation of AD system biogas purification filter. Three different conceptual designs were generated from possible design consideration, feasibility study and preliminary test and with the help of decision matrix; the best conceptual design was selected from which the purification filter was fabricated. The selected concept for detail design was a transparent polyethene cylindrical purification filter fitted with local iron sponge containing activated charcoal and local potash. The reagents were arranged in this order; local potash for the removal of water vapour and carbon dioxide followed by activated charcoal which serves as a purifying agent for hydrogen sulphide. The results obtained showed reduction in percentage composition of hydrogen sulphide (H_2S), carbon dioxide, and water vapour. On the other hand, there was an increase in percentage composition of methane (CH_4) which is an indication of improvement in methane production after purification. The outcomes of the results obtained were satisfactory and the combination of local potash and activated charcoal was adequate for biogas purification.

Sah (2013) studied a packed bed scrubber for upgradation of biogas using a closed-loop process and observed that By using a packed bed scrubber with granite packaging and algal culture, the biogas was purified and after purification the methane percentage increased by approximately 27% and the CO_2 decreased by 77%. And H_2S decreased by about 94%.

Kismurtono (2011) studied the biogas purification in packed column with chemical absorption of CO_2 for energy alternative of small industry. Research design and methods used to test removal of the CO_2 from biogas stream. Under continuous operation condition, first the biogas introduced at the bottom of the packed column, passing through the aqueous NaOH 1M solution, flowing downwards to the solution separator. In this column the CO_2 is absorbed and transformed into aqueous NaOH 1M solution. Samples of the inlet and outlet biogas were taken during experimental tests using gas samples. The compositions of these samples were determined by gas chromatography. This research studied the effect of pressure, concentration of aqueous NaOH 1 M solution in inlet absorbent and temperature on percentage of CO_2 absorbed. Liquid flow rate was 40 ml. S^{-1}, pressure was varied 350 and 700 mm H_2O. The gas flow rate was held constant at 600 ml. S^{-1}.

Jan Cebula (2009) found that to upgrade biogas to bio CNG first of all sulfur must be removed from biogas. It is to be carried out first because most processes of CO_2 removal from biogas act antagonistically towards hydrogen sulfide; the smaller concentration of hydrogen sulfide, the better effects of carbon dioxide removal from biogas. H_2S removal can be done in the same process line used for CO_2, but it should be done first.

Other Biogas purification system and technologies

Srichat *et al.,* (2017) studied the biogas purification system using Calcium Hydroxide and Amine solution. The liquid spray absorption tower was used to purify the biogas from layer chicken manure. The solution used in the experiment were 5 types which were 1) pure water 2) Calcium hydroxide 0.1 mol, 3) Calcium hydroxide 0.2 mol, 4) Mono Ethanol Amine (MEA) 0.1 mol and 5) Mono Ethanol Amine (MEA) 0.2 mol. The solution flow rate was fixed at three levels: 10, 20, and 30 l/min and the biogas flow rate was fixed at 5, 10, and 15 l/min. The solution flow rate was fixed at three levels: 10, 20, and 30 l/min and the biogas flow rate was fixed at 5, 10, and 15 l/min. Tests on biogas treatments with an mono ethanolamine solution with concentrations of 0.1 and 0.2 mol. resulted in the highest methane levels of 81.5% and 77.2%, respectively. The highest level of methane (89.3%), produced from this experiment, occurred when the biogas flow rate was 5 l/min. and solution flow rate was 30 l/min.

Mostbauer *et al.,* (2007) found that it was proposed that municipal solid waste incineration ash (MSWI bottom ash) could be used for removal of CO_2 and H_2S from landfill gas (LFG) or biogas. Several experiments at the technical scale demonstrated that ash-based enrichment of CH_4 in biogas and lean landfill gas. Pilot tests on biomass-ash based upgrading of biogas did not yield a constant gas composition of the purified gas. However, a long-lasting removal of H_2S (up to 34 days) was observed, and therefore wood ash (and similar biomass ashes) may be used as a trap for removal of hydrogen sulfide from biogas in small and medium biogas plants, however they could not be used for CO_2 trap only since high filter rates, make this option is not economically feasible.

Vinayak (2014) developed a design of Biogas Scrubbing, Compression & Storage System. The scrubbing unit consists of the following sub units i.e. CO_2 separation unit, H_2S separation unit and Moisture separation unit. The raw biogas is first passed through a CO_2 separation unit. Limestone crystals are used to remove carbon dioxide. Limestone reacts with carbon dioxide to form calcium carbonate. Hydrogen sulphide is removed by using catalyst iron oxide in the form of oxidised steel wool or iron turning from any workshop. Once biogas comes in contact with this wool, iron oxide is converted into elemental sulphur. Finally the biogas is passed through a moisture separation unit. Here silica gel crystals are proposed to separate moisture. Silica gel crystals should be replaced after a specific time according to the rate of purification.

Ejiroghene *et al.,* (2016) studied that the quantity of impure biogas evacuated for percentage composition analysis was 4kg. This was divided into four different storage containers (1kg each) and four different purification tests were carried out with activated charcoal and potash. The same quantity of activated charcoal and potash each measuring 250g was used. The results of the purification with Activated charcoal and Potash were show that the percentage composition of hydrogen sulphide (H_2S) decreases from 0.57% to 0.01-0.02%, carbon dioxide from 31.00% to 18.61-18.95%, water vapour from 0.93% to 0.01-0.03% and for methane (CH_4), it increases from 67.50% to 81.00-81.35%. The increase in the percentage composition of methane, decrease in the compositions of carbon dioxide, hydrogen sulphide, and water vapour shown the purification filter performance was efficient.

Shah (2015) developed and studied low cost biogas purification system for application of bio CNG as fuel for automobile engines. The experimental work is carried out at biogas research centre of Gujarat Vidhyapeeth at Sadra having a biogas plant of Deenbandhu Model of capacity 3 meter cube per day. Four plastic bottles with necessary pipe fittings were used in this experimental work. Raw biogas first enters from bottom of the first chamber containing iron feelings and comes out from top. This will remove H_2S and somewhat moisture. In second chamber solution of NaOH with water is prepared with concentration of 40 %, due to exothermic reaction very high amount of heat is produced. Gas is allowed to bubble in that solution and certain amount of H_2S and CO_2 will get removed. In third chamber solution of $Ca(OH)_2$with water is prepared with concentration of 40 %.Gas is allowed to bubble in that solution and certain amount of CO_2will get removed. For this experiment, blue silica gel was used. Biogas will enter from bottom and will come out from top of the chamber. This will remove moisture from biogas.

Conclusion

In this review study it has been observed that the biogas is constituted of different component gases the majority of them being methane (CH_4), Carbon Dioxide (CO_2) with traces of Hydrogen Sulfide, and moisture. Raw biogas contains so many impurities. Among which removal of carbon dioxide, hydrogen sulfide and moisture are important for upgrading biogas for various application. The presence of H_2S makes biogas corrosive to metal parts. Carbon dioxide is present in raw biogas with very high concentration. This decreases energy content per unit mass /volume and limits its use for low quality energy applications. Presence of moisture in biogas to be used as fuel may corrode metallic parts of engine and fuel supply system. The purification of biogas is essential so as to achieve more effective utilization. This can be achieved by using various materials i.e. limestone crystals, iron turnings/iron oxides, activated carbon, silica gel, granite, algal culture etc. Use of low cost materials is desirable.

References

Antonio-Abdu Sami M. Magomnang, and Prof. Eliseo P. Villanueva.2014. Removal of Hydrogen Sulfide from Biogas using Dry Desulfurization Systems. International Conference on Agricultural, Environmental and Biological Sciences (AEBS-2014) April 24-25, 2014.

Divyang S. and Hemant N. 2015. Low Cost Biogas Purification System for Application of Bio CNG as Fuel for Automobile Engines. In. J of Innovative Science, Engineering & Technology, 2 (6), 308-312.

Ejiroghene K.O., Oghenero W.O. and Eruero V. A. 2016. Performance Evaluation of Design AD System Biogas Purification Filter. 3 (2016) 17-27.

Ejiroghene Kelly Orhorhoro, Oghenero Wilson Orhorhoro, Eruero Victor Atumah. 2018. Performance Evaluation of Design AD System Biogas Purification Filter. International Journal of Mathematical, Engineering and Management Sciences 3(1) 17–27, 2018ISSN: 2455-7749.

Jan Cebula: Biogas Purification by sorption techniques, "Architecture, Civil Engineering, Environment, The Silesian University of Technology no. 2/2009.

Kui Zhou, Somboon Chaemchuena, b, Francis Verpoort.2017. Alternative materials in technologies for Biogas upgrading via CO_2 capture. Renewable and Sustainable Energy Reviews 79 (2017) 1414–1441.

M. Fernandez-Delgado Juarez, P. Mostbauer, A. Knapp, W. Muller, S. Tertsch, A. Bockreis, H. Insam. 2017. Biogas purification with biomass ash. Waste Management. 10.1016 (2017) 0956-053.

Manjula D.G. and Mahanta P. 2016. Biogas Purification using Chemical Absorption In. J. of Engineering and Technology 8 (3) 0975-4024.

Michael, Jason, Peter and James Faupel, "Design and Development of a Biogas compression and storage system capable of implementing in the developing world", Department of Mechanical, Materials and manufacturing Engineering

Mojica E. E., Ardanielb S., Leguidc J.G., and Andrea T. L. 2017. Development of a Low- Cost Biogas Filtration System to Achieve Higher-Power Efficient AC Generator In. Conference on Engineering and Technology 1930(020042)1-7.

Mostbauer, P., Lenz, S., 2007. Utilisation of lean landfill gas using MSWI bottom ash. In: Cossu, R., Stegmann, R. (Eds.), 11th International Waste Management and Landfill Symposium. CISA, IT, Cagliary, IT.

Muhammad Kismurtono. 2011. Upgrade Biogas Purification in Packed Column with Chemical Absorption of CO_2 for Energy Alternative Of Small Industry (UKM-Tahu). International Journal of Engineering & Technology IJET-IJENS Vol: 11 No: 01 59 114501-0808.

N. Tippayawong, P. Thanompongchart. 2009. Biogas quality upgrade by simultaneous removal of CO_2 and H_2S in a packed column reactor. Energy. 35 (2010) 4531-4535.

S.S Kapdi, V.K. Vijay, S.K. Rajesh, Rajendra Prasad "Biogas scrubbing, compression and storage: perspective and prospectus in Indian context". Centre for rural development and technology, Indian Institute of Technology, New Delhi 110 016, India.

Vinayak R.G., and Katti P.K. 2014. Design of Biogas Scrubbing, Compression & Storage System J. of Electrical and Electronics Engineering 2278-1676 (2320-3331) 58-63.

Virendra K. vijay, Ram Chandra, Parchuri M. V. subbarao and shyam S. kapdi, "Biogas purification and bottling into CNG cylinders: producing bio CNG from biomass for rural automotive applications". Mechanical Engineering department, Indian Institute of Technology, Delhi, Hauz khas, New Delhi- 110 016, India.