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A Retrospection on Current Trends in Biogas Purification

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***Abstract:** As the non-renewable resources are depleting at a lighting speed there will be crisis for requirement of energy in near future. The only alternative is to go for renewable resources. It has been proven that biogas and gasoline can be used with association to reduce the energy demand. As even though electric vehicles are booming in the market, it will take more than a decade to move towards electric world, especially in India. The reason behind that is, the raw material required to make batteries is not at all available with India, so the only option is to export, which imposes additional cost on the country's financial books. And also the tendency of common Indian pupils to shift from IC engine to electric vehicles will incur a high debt. So to reduce the dependency on electric vehicle and also to reduce cost, biogas in the form of compressed natural gas is the only way to come in near future. The motivation of this review work is to produce biogas from food wastes, to purify and store in cylinder used to run vehicles and to analyze the effect of performance and emission characteristics of an engine.*

***Keywords**: Biogas purification, CH_4, CO_2, H_2S, O_2 and water vapor*

I. INTRODUCTION

1.1 Background

From the last 10 years of historical data it can be seen that in near future the dependency on fossils fuel will end and demands on renewable with increase. Waste management has become a very important factor for all, especially for urban India. Day by day increasing population leads to a lot of waste generation and so its proper utilization and management have become a need of the hour. Out of total world renewable resources only 1.5% of the share is of biogas, but since 1990 it has increased to 15% per year. As the price increasing and quantity is decreasing of crude oil, it imposes economic constraints on developing countries.

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Also the demand of energy for all sectors have been increased drastically leading to more generation of waste and use of non renewable resources, so to meet the energy demands there is a need to explore more options in the field of renewables.
The main content in biogas is methane, which is produced due to anaerobic digestion of bacteria in the absence of oxygen. The main components of this process are a digest residue and an energy-rich biogas. [1]

1.2 What is Biogas?

Biogas as the name suggests bio means a life that is a microorganism which is produced from a lot of different organic raw materials and used for various energy services, which are renewable. Practice of production and use of the gas from biogas is widely used all around the world, due to lot of advantages. Biogas is produced in the absence of oxygen, so called as anaerobic digestion or AD. The raw material for biogas includes, waste which is biodegradable, for example municipal and agricultural wastes (having maximum gas producing capacity). There are lot of variation in the shape, size and technology of biogas production done all round the world, of which some includes fixed and floating drum type of biogas plants. As biogas has CO_2 and H_2O content in it with methane being maximum, the flame temperature of biogas decreases due to its presence. [2] Biogas consists of methane (40-80%), carbon dioxide (30-40%), small quantities nitrogen and hydrogen sulfide. Among the biogas constituents methane is flammable. Biogas has a heating value of 13720-27400 kJ/m3. Biogas has very low flame speed of 0.3 m/s and specific gravity of 0.554 [3].

1.3 Biology of Biogas

The process of digestion consists of four steps, which is processed by different groups of bacteria. The larger organic polymers are broken down into smaller ones like fatty acids, amino acids, simple sugars and water by hydrolysis phase, which is the first step of digestion. In second phase of digestion the material is converted into fatty acids, alcohols, carbon dioxide, hydrogen and ammonia by a phase called as acidogensis. The third phase is acetogenesis where the organic acids are formed which is the path way to fourth phase i.e., methanogenesis. In the methanogenesis process methane is produced. About 90% of total amount of methane is formed during this phase, while a raw biogas has about 50 and 60% of methane content.

The use of diesel fuel in C.I. engine emits pollutants such as CO, CO_2, NO_x and HC in the exhaust gases. The quantity of pollutants depends on the combustion temperature and type of fuel used. These pollutants have adverse effects on human health and the environment (Sastry, C.A.).

Therefore it has become necessity to use renewable fuels to reduce emissions. Biogas is one of the renewable fuels to be used in C.I. engines. Due to the low cetane number and high auto-ignition temperatures, biogas cannot be used alone in C.I. engine. Hence, the dual fuel technology in C.I. engine plays important role for use of gaseous fuels.

During a dual fuel mode of operation, air-biogas mixture is aspirated and compressed in a traditional diesel engine and is ignited by diesel fuel injection at the end of compression stroke. A diesel engine can be converted in to a dual fuel engine with minimum modification at the inlet manifold of air through which air-biogas mixture enters in to the engine cylinder [4].

1.4 Biogas Applicability and Production

Biogas been a low cost fuel widely used in India for cooking purposes mostly in rural areas, while also been used as alternative for gasoline now-a-days. Production of electric energy using biogas as a fuel is also in practice in most parts of the world, including India. The burning capacity of biogas is high when the percentage of methane in it is more as discussed earlier, so acts as a substitute for petroleum industries. Only the problem associated is of storage as biogas occupies large volume so storage is an issue.

II. A BRIEF LITERATURE REVIEW

Biogas is the only solution to reduce the increase in global warming, which helps in the use of alternative fuels for most used commodity that is vehicles. Wastes form kitchen is a rich source of biogas used for both domestic and commercial usage. As the gas produced in biogas digester has a mixture of many unwanted gases the focus in literature would be on the improvement in the quality of the useable gas, which indirect helps to reduce and reuse the gases which are taken away while filtering the unwanted ones. The literature review will focus on anaerobic digester, Biogas digester types and technical parameters which affect the quality of methane (pH and alkalinity), increase in production of methane gas using various technologies, biogas application in IC engine and its energy analysis

The calorific value of gas, produced from a biogas plant is an attractive choice for renewable to be as an alternative fuel which helps to reduce dependency of mankind on non-renewable. The data from the membrane based plant was compared with the actual plant and found increase in the purity of methane percentage. The final data of carbon dioxide and methane content at each stage with ANOVA techniques helps to attain correlations. This analysis helps to quantify the solution to recover the methane gas, techniques like increasing the effective thickness. Also in near future more advanced techniques like artificial neural network will help in getting more methane out of biogas resource [5]. The upgrading of combustible biogas using a carbon hollow fiber membrane comparing with polymeric membrane from commercial aspect was done by Shamim [6] and modification of the carbon hollow fiber membrane was recorded as per the experiment testing done using Aspen HYSYS. The percentage of pure methane depends on the feed to the digester, which varies from whether it is agricultural or food waste. About 50 to 70% methane is produce from cow manure, which is the maximum amount due to anaerobic digestion. Chicken manure also has the same percentage as that of cow manure. The paper showed that animal waste have a higher potential of producing renewable energy and in Malaysia animal waste is also available at low cost which proves helpful for the generation of biogas energy and electrical power [7].

Low energy consumption membrane was used to separate volatile gas that is methane from the raw biogas, so membrane was used to separate the gas which also acts as an adsorber. A membrane made up of polyimide hollow fiber was used as from the previous work [8]. The membrane used provided high adherence for separating CH_4 from CO_2, H_2S and H_2O. The results showed that the percentage of biogas was increased by 20%. Purging of gas also suggested an option for increase in the percent of methane of up to 90%.

A drastic increase in combustible gases was seen using a capillary module with polyimide membranes was used to increase the percentage of methane form 55 to 91%. The membrane used was resistant to sour gases which reduced H_2S and water vapor contents, but for CH_4 requires hybrid system, as it increases its efficiency. Experimental data showed the potential of membrane based technology for biogas purification [9]. As suggested by the author on site experiments with real biogas from anaerobic fermentation is required. Cellulose acetate membrane was tested for many situations to study the permeability of each gas like CH_4, H_2S, and CO_2. These membrane was the best suited for this purpose for all conditions of pressure and temperature. Acetate based membrane were tested further for its efficiency to remove CO_2 and H_2S from a mixture of CH_4, CO_2 and H_2S by approximating biogas. For the temperature, pressure and stage cuts being tested, the best separation occurred at 25°C, 550 kPa, and 0.45 respectively [10].

Pressure Swing Adsorption membrane (PSA) was used as a medium to separate the methane and carbon dioxide present in biogas in this paper. Langmuir isotherm model helps to get the amount of pure gas from the adsorption column. The pressure and purge gas ratio helps in the adsorption and plays an important role to improve the purity of biogas. A stepwise PSA process helps to recover pure methane from a mixture of CH_4 and CO_2 [11]. Zeolites are such materials which don't harm environment and hence are of utmost important for biogas purification. As they have good resistance to temperature and high cation exchange capabilities, so prove as good adsorbents for biogas [12]. The effect of pressure, temperature and water particles was studied and it showed that CO_2 adsorption increases with increase in pressure and decrease in temperature while water particles decrease the efficiency of adsorption [13].

Zeloite capability is determined on the basis of the pore size it possesses, such as micro and macro pores and in this part is mostly microporous adsorption events occur [14].

A heavy testing of adsorption for desulfurization is done in this paper to protect the catalytic methanation reactor during the production of methane from biogas. Both biowaste and wastewater were used as a raw material for biogas production. The harmful traces in biogas was removed in two stages, first stage included the removal of H_2S, while second stage includes the removal of trace of organic sulfur compound and siloxanes. On the basis of the location and local requirement specialized solutions required for the plant to function are decided on site itself. A mixture of biogas slurry from waste water and biowaste digester was used to test the performance of catalytic methanation reactor. Using this removal of hydrogen sulfide gas was tested by a gas adsorption method [15]. There is a need for upgrading of biogas technology as the challenges faced in the sector are in terms of energy consumption and operating costs. This paper reviews the cleaning and upgrading technologies for biogas for increasing its purity, methane recovery and cost analysis. Newly developed technologies such as cryogenic separation, hydrate separation and in-situ upgrading are coping up with near future, but the testing and information related to it is available only on small scale or laboratory tests, so more efforts needs to be made for the same. Use of CO_2 for other purposes reduces the cost of biogas purification, which in turn can generate revenue [16]. The paper focuses on membrane based technology used for separation of biogas specifically CH_4. The review paper will only focus on polymeric materials. The membrane based technology is thoroughly reviewed in this paper by distributing the work in the performance parameters such as commercial, lab-made and mixed matrix membranes. Also the effect of variation of many other parameters on membranes is studied in this paper which ultimately decides the performance and life span of the technology [17].

A PVA blend membrane was experimentally investigated in the study. The PVA membrane supported the transport of biogas and helps to remove CH_4 from CO_2 with high efficiency and stability. The recovery of CH_4 was up to 99% at low running cost; as the water vapor is an added advantage for CO_2 permeation no pre treatment is required for its removal. The simulation of the membrane was conducted in Aspen HYSYS1 which showed that a 2-stage-in-cascade configuration has the highest separation efficiency [18].

The separation of CO_2 from biogas is the major perspective for cost estimation. The methane content can be increased by recirculation of a liquid stream from CO_2 absorption process and return back to the digester. Varying the pressures methane percentage improvement is tested using synthetic feedstocks. According to Henry relationships the pH and pressure are the most important parameters while considering CO_2 desorption [19]. The use of in-situ method for biogas purification, in vehicle fuel was done using desorption of CO_2 using computer simulation. The results showed no impact on CH_4 productivity activity. The variation flow rate of sludge varies the methane content in the desorption column [20]. By continuous addition of hydrogen in the biogas reactor, a high level and quality of biogas production can be achieved. Also the content of biogas can be seen around 95% at steady state and can be maintained at so by keeping the stirring speed constant. Enrichment under thermophilic condition provides higher CH_4 production by removing H_2 and CO_2. Usually biogas is upgraded or its performance is increased by water washing, pressure swing adsorption, poly-glycol adsorption, and chemical treatment, but the above all involves cost which reduces its effective use in normal application [21].

The extended granular sludge bed generates biogas is recirculated through carbonation process and after purification the process of calcium removal from the leachate is carried out. Optimization is done by $CaCO_3$ precipitation. Calcium concentration of 181-375 mg/L in leachate and methane content of 87.1-91.4% in biogas results in p^H of 10-11.

Different method for calcium removal from leachate

1) MSW Leachate –In this method calcium from the leachate is removed from metal components in it.
2) Experimental apparatus and configuration and operation- in this method gas laboratory apparatus is used with a definite configuration with bio-reactors maintained that $34\text{-}37^0$C and the calcium are obtained from it. Caustic soda is used to maintain p^H.
3) Batch trial- in this method calcium is removed from batches after particular time interval.
4) Continuous trial- in this method the calcium is extracted continuously from leachate flow [22].

III. DETAILED BIOGAS PLANT TECHNOLOGY ANALYSIS

The improvement in separation performance reduces the energy consumption and cost of membrane separation system. The membrane separation technology has a great importance in these years. The numbers of process are being invented for CO_2 separation. The performance of membrane is mainly dividing by using two basic characteristics - Permeance and selectivity. Mathematical modeling and experiment testing are two investigating methods of membrane based gas separation processes. As this process skid-mounting so, it gets easily installed. This process has low capital cost and low energy consumption. Complete separation of CO_2 is obtained hence the high product purity is obtained. But due to this process emission of corrosive solvent to the environment is observed [23]. For increasing of biogas production, food and restaurant wastes are used in the Slovak; the volume of fermentation tank is nearly 162000m$^{3.}$ But daily biogas production is very less nearly 51.500m^3. From long time research, the result shows that, higher biogas production produce from food waste in average 930L of biogas of 1 kg. Methane produce from different food wastes at 37$^{\cdot}$c and in 28 days of digestion time. The variation over daily and weekly of food waste are measured over a two- month period. The batch type feeding of anaerobic digestion test is used to evaluate the anaerobic digestibility and biogas and methane yields. Food waste contain well balance nutrient for anaerobic microorganisms. We get methane after 10 and 28 days of digestion.

Production of biogas was measured in biogas flow meter.
Biogas production during the long-term tests with food waste as feedstock is around 930l of biogas from 1 kg VS of food waste and 52.5% of methane. We get 60-65% of methane from sludge .and 55-60% of methane from sludge and food [24]. For utilization of biogas, there are several methods to collect CO_2.for the best option we have to compare three retrofits from both technical and economic views. SYS-I is use to collect CO_2 from raw gas and produce bio-methane instead of electricity and heat, SYS-II is use to collect CO_2 MEA- based chemical absorption after combustion of biogas. SYS-III is use to collect CO_2 from oxy-fuel combustion of raw gas. For 2 degrees increase in global temperature carbon negative technologies are necessary. Biogas is a cleanest renewable fuel for transportation. Raw biogas contains methane and CO_2. And for upgrading process it is important to remove CO_2.It is important to see that for between the two solutions with heat and power [25]. Anaerobic digestion of organic biodegradable materials is use to produce biogas it contains impurities like carbon dioxide (CO_2), hydrogen sulphide, and other trace gases so its application is limited. Chemical absorption is able to produce gas which contain large amount of methane above 95% and there is no methane loss, so it is mostly used in large scale application. For cleaning the biogas, sodium hydroxide is use. About 60% was the highest removal efficiency being observed. We can produce energy from different renewable sources such as solar energy, hydropower, wind power geothermal, biofuel and biomass. Biomass is very suitable source for energy supply for biogas production. Anaerobic digestion of organic biodegradable waste is used to produce biogas. The digestion is dry as well as well both having advantages and disadvantages. Use of biogas is limited because it contains impurities [26]. The production of bio-methane gives a wide application in heat and power generation as well as vehicular fuel. The market condition for upgrading biogas has changed in few years ago. The potential utilization of biogas is more useful to convert into bio-compressed natural gas, as well as storage systems are investigated in depth. For storage purpose buffer and cascade storages are been used based on having same fuel economy and less carbon dioxide (CO_2) emission for bio-CNG. Anaerobic degradation of organic compounds is used to produce biogas it contains three main elements that is methane, carbon dioxide (CO_2), and nitrogen [27]. Biogas consist 55-60% methane 38-40% carbon dioxide 1-2% water-vapor and other remaining contaminated. The demand of bio-methane increasing day by day so numbers of method are increases to remove CO_2 from biogas which is chemical or physical absorption liquid such as methanol, pressure swing absorber or membrane separation technology. Before 10 years, membrane technology has emerged for separation of CO_2. The membrane module is sensitive to impurity. Due to this produced high purity methane. It is a single step method of raw biogas purification [28]. A lingo-cellulose-based activated carbon has adsorption on it and separates CO_2. From various methods of biogas upgrading Pressure Swing Adsorption (PSA) is very effective technique for Indian conditions due to its low cost and high energy efficiency. To remove CO_2 zeolites and activated carbon proved to be effective for its separation. In the study the adsorbent material being selected is a biomass-based activated carbon produced from a low cost biomass precursor, pine saw dust.The study shows the various experiments conducted on the biogas streams under dry and wet conditions by use of pine sawdust activated carbon for the separation of CO_2 from raw biogas streams, so it is best suited for CO_2/CH_4 separation at atmospheric pressures without the need of removal of water molecules [29]. Biogas is an eco-friendly fuel, now a days it only used for household purpose and not ready for transportation. To make it transportable there is need of removing the CO_2, H_2S and moisture from the raw biogas, so that biogas can be compressed and filled in the cylinders. Various Adsoprtion, membrane based and cryogenics technique are studied for CO_2 removal from the mixture of raw biogas and for H_2S like dry oxidation process, introducing oxygen in the biogas, adsorption using iron oxide, liquid phase oxidation process etc. The study stresses the importance of compressing the biogas so that it can be used as CNG fuel for vehicles. It shows the data economical feasibility of producing compressed bio-CNG in Delhi [30]. Use of an additional external pressure is important to get purified combustible gas, which is done using water scrubbing technique. Biogas is produced by using anaerobic digestion process for treating wastewater or solid waste. Generally biogas composed 50-75% methane 25-50% carbon dioxide 0-10% nitrogen gas 0-3% hydrogen sulphide 0-1% hydrogen gas and remaining other gaseous. Several methods are used to purify biogas such as traditional absorption upto advanced cryogenics one's. By considering various parameters we can select appropriate method for purification. Water scrubbing at high pressure is most commonly used technique for biogas purification, but the disadvantage is it requires higher electricity consumption. Packing carrier is installed in water scrubbers to increase transfer efficiency between gas and liquid phase. It gives purified gas with more than 90% methane. Use of mathematical modeling for high water retention proves to be useful technique for biogas purification [31]. To increase the biogas various methods have been invented. By adding some additives increase the growth of bacteria and decrease unwanted effects. As per the recent research done by Menon, adding Ca, Mg, Co and Ni increases the biogas yield by 50%, but there is a disadvantage it required high cost for such elements. By considering cost it required cheaper additives Huilinir el at. Use fly ash as an additive. It also suggests that for improving the percentage of biogas the addition of drinking water treatment sludge (DWST). Drinking water treatment sludge contain the various contain it makes it cheap mixture for biogas production. By uses of DWTS method 59% improvement in a biogas formation. DWTS also reduce lag phase and retention time. It has been observed that the highest percentage of methane obtain when 6mg/kg DWST added [32]. The liquefaction of biogas can also be produced form LBM which has a higher energy density than the other fuels. Liquid bio-methane is three times more energy dense than compress bio-methane. It is used for the longer vehicles antimony.

It I made from wastes and recycled material but there is no food-waste present. When the uses of bio-methane as a vehicles fuels end it convert in to liquid biogas it is more profitable because the LPG is more efficient compared to biogas at atmospheric pressure. LPG is produced by two methods, a low temperature upgrading technique and the conventional small scale liquefaction plant. Experimental results showed that low temperature techniques give results same as the advanced technique of cryogenics as its saves a lot of energy. One more advantage of the low temperature technologies that is that, CO_2 is obtained as a clean liquid produced and it can be used for further applications [33].

IV. DISCUSSION FROM LITERATURE

The purpose behind purification of biogas is to increase the percentage of the combustible gas available for use, which might affect the end users. Carbon dioxide the main impurity needs to be removed from the biogas. Various purification technologies have been discussed in the above literature ranging from water scrubber to highly advance cryogenic's. Among the various alternative technologies present for biogas purification chemical scrubbing proves to have the highest biomethane purity level. But each available technologies proves to have its pros and cons in appropriate share, as seen in table 1, so it's important to focus on technology as well as cost of it. Membrane based purification technology adhere to both of the above said parameters, but still needs to be more researched.

Table 1: Available technology for biogas purification

Technique	Advantages	Disadvantages
Water Scrubbing	1. Very low electricity consumption 2. Losses of combustible gases less than 2% 3. High efficiency	1. less flexible technique 2. Investment is high. 3. OC and OMC is also comparatively high. 4. Large volume of water consumed.
Organic Scrubbing	1. High retention of methane gas (>97%) 2. Less space required for installation 3. With a prior pretreatment remove unwanted gases	1. High operation cost incurred. 2. Difficult operation to be performed. 3. Regeneration problem faced by organic scrubbing.
Chemical Scrubbing	1. Highest combustible gas percentage being obtained (>99%) 2. Cheap operation cost 3. Low level of methane losses.	1. Regeneration requires high energy demand. 2. Foam formation causes heat transfer problems 3. Corrosion problem due to chemical being present.
Membrane Separation	1. Simple to construct 2. Less OC and OMC required. 3. Highly reliable technique 4.low level losses of methane gas	1. Requires multistage to get more combustible gas 2. Life span is short. 3. High cost of membranes 4. Restricted use for a specific type of waste.
Pressure Swing Adsorption (PSA)	1. High efficiency suitable for Indian condition 2.A compact technology 3.Low energy consumption 4. Impurities can be easily handled.	1. High capital required 2. OC and OMC is higher 3. Loss of combustible gases is more 4. As compared to other techniques less efficient.
Cryogenic Separation	1. Highest level of purity attained 2. very low losses of combustible gas 3.High purity of CO_2 obtained	1. Very much expensive technique. 2. Highest energy consumption as compared to other techniques. 3. Pretreatment is a necessity 4. Can be implemented only on large scale

V. CONCLUSION

The answer to the energy challenges faced by any country is to create more dependency on renewable, such as biogas. The combustible biogas can be an alternative for renewable been used extensively now-a-days. This paper reviewed the available technologies for the purification of biogas to produce a combustible gas from it. The selection of appropriate purification technology mainly depends on the atmospheric conditions and cost estimation. The PSA technology is preferably most suitable for Indian conditions and hence is the answer for the purification techniques available for combustible biogas. Recent available In-situ and cryogenic biomethanation techniques are highly costlier and hence produces an obstruction for implementation.

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