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Biogas to Biomethane: Upgradation Technologies

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Biogas is the mixture of gases produced by the breakdown of organic matter in the absence of oxygen (anaerobically), primarily consisting of methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulfide (H_2S), moisture and siloxanes. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. Biogas is a renewable energy source. Biogas is produced by anaerobic digestion with methanogen or anaerobic organisms, which digest material inside a closed system, or fermentation of biodegradable materials. This closed system is called an anaerobic digester, biodigester or a bioreactor. The gases methane, hydrogen, and carbon monoxide (CO) can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel; it can be used for any heating purpose, such as cooking. It can also be used in a gas engine to convert the energy in the gas into electricity and heat.

Table 1: Composition of Raw Biogas

Compound	%
Methane CH_4	55–65
Carbon dioxide CO_2	35–45
Nitrogen N_2	0–10
Hydrogen H_2	0–1
Hydrogen Sulfide H_2S	0–3
Moisture	Saturated
Average calorific value of biogas is 20 MJ/m³ (4713 kcal/m³)	

Biogas Upgradation/Enrichment

Enrichment method of biogas is the process of removing unwanted gases (CO_2, H_2S, and water vapor) from biogas to increase the calorific value, so it is more economical to compress and transport to longer distribution or move to other area. The CO_2 and H_2S removal can increase the percentage of biomethane in biogas. Raw biogas produced from digestion is roughly 60% methane and 29% CO_2 with trace elements of H_2S; it is not high quality enough to be used as fuel gas for machinery. The corrosive nature of H_2S alone is enough to destroy the internals of a plant. The solution is the use of biogas upgrading or purification processes whereby contaminants in the raw biogas stream are absorbed or scrubbed, leaving more methane per unit volume of gas. Biogas cleaning is important for two reasons: (1) to increase the heating value of biogas, and (2) to meet requirements for some gas appliances (engines, boilers, fuel cells, vehicles, etc).

Table 2. Effects of impurities in biogas

Gases	Effects
Carbon dioxide (CO_2)	• Inflammable gas, decreasing calorific value • Corrosion (contain carbon acid) if biogas is in wet condition
Hydrogen sulfide (H_2S)	• Inflammable gas, decreasing calorific value • Corrosion • Poison
Ammonia (NH_3)	• Emits NO_x emission after combustion • Anti-knock properties of engines
Water vapor	• Corrosion
Nitrogen N_2	• Decreasing calorific value • Antiknock properties of engines

Biogas Enrichment Processes

- Purification
- Compression
- Bottling

Purification

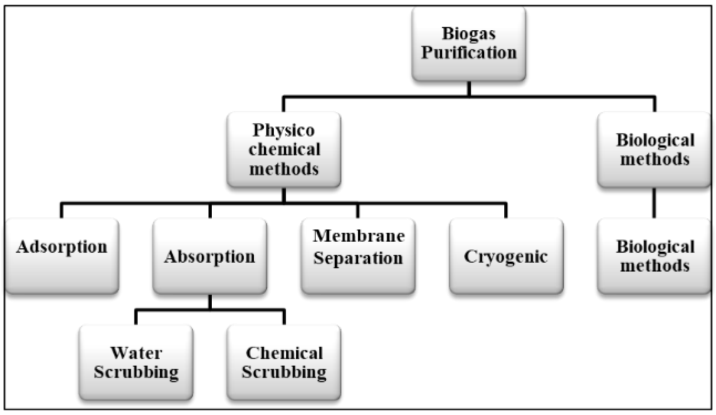

Fig. 1. Biogas purification methods

Biogas purification is a process of removing the impure gases in biogas that affects the gas transmission grid, appliances or end user, and the increasing calorific value. The impure gases are carbon dioxide, hydrogen sulfide, nitrogen and trace elements. The increase of calorific value affects the increase of biogas energy efficiency so it is able to compete with fossil fuel-based energy. There are many methods of biogas purification that have been developed and shown in Figure 1.

Absorption

In the absorption technique of biogas purification, the raw biogas is brought into contact with nonvolatile liquid phase. The purpose is the mass transfer of contaminant from the gas phase to liquid phase. The main idea in cleaning biogas using absorption is to transfer carbon dioxide to stationary liquid phase. There are two types of techniques depending on the types of the absorbent:

a. Water scrubbing: Water is used as solvent in scrubbing. The solubility of methane in water is much lower than that of carbon dioxide and hydrogen sulfide. In principle, carbon dioxide and hydrogen sulfide can be removed. However, because hydrogen sulfide is poisonous and dissolved hydrogen sulfide can cause corrosion, the pre-treatment of waste is required. The disadvantage of this method is the large amount of water needed so it must be treated in wastewater to minimize the water consumption. Water scrubbing is the most commonly used method to clean biogas, and plants are commercially available in a broad range of capacities.

b. Chemical scrubbing: It is very similar to water scrubbing. The difference is that the carbon dioxide is absorbed in chemical solvent. Chemical scrubbing involves the formation of reversible chemical bonds between the pollutants and the solvent. The chemical solvents used in biogas cleaning are alkaline solutions such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and alkanolamine solutions such as mono ethanol amine (MEA), di-methyl ethanol amine (DMEA) or tertiary amines. In carbon dioxide absorption by chemical solvent, the following reactions take place as given in Eqs 1 to 3.

$$CO_2 + 2\,OH^- \rightarrow CO_3^{2-} + H_2O \quad \text{..... (1)}$$

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO^{3-} \quad \text{..... (2)}$$

$$CO_2 + R - NH_2 + H_2O \rightarrow R - NH_3^+ + HCO_3^- \quad \text{... (3)}$$

The advantage of this method is that the solvent can be regenerated. However, the downside of this technology relates to the energy consumption to regenerate the chemical solvent.

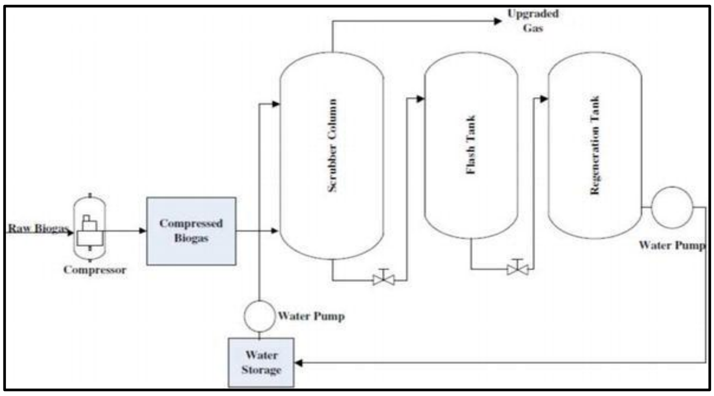

Fig. 2: Schematic of chemical scrubber

Membrane technology

Membrane technology is a separation method at molecular scale. In biogas cleaning, carbon dioxide and hydrogen sulfide can be removed selectively through membrane column so it is able to enrich methane component in biogas. Membrane used in this technique is made of materials that are permeable to carbon dioxide, water, ammonia and other contaminants.

Adsorption

Adsorption is a method to separate certain gas from gas mixtures based on the affinity to a solid adsorbent. In biogas purification, the adsorptive materials are zeolite, active carbon, silica gel for carbon dioxide and hydrogen sulfide adsorption. The adsorption process relied on the fact that at low pressure, gases tend to be attracted to adsorbent and at higher pressure, more gas was adsorbed.

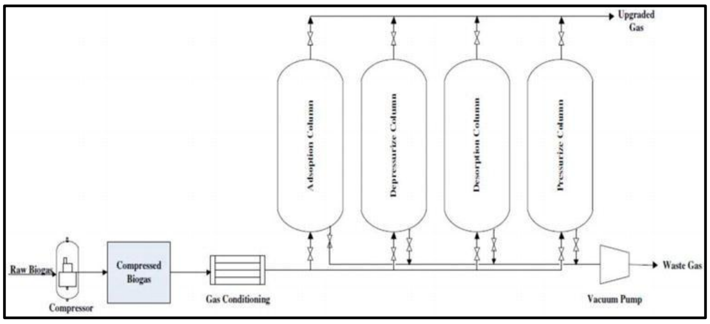

Fig 3: Schematic of adsorption in biogas purification

The advantage of adsorption method is that when solid adsorbents are saturated, it can be replaced by regenerated adsorbent by washing with water or heating at high temperature.

Physical-chemical biogas purification is the most commonly and frequently implemented method. Table 3 shows the results of evaluation of biogas purification method by many researchers. Regarding the technology adoption, biogas purification technology that requires a lot of operations is always not sustainable in rural areas or developing countries. Therefore, a cheap and easy biogas purification method needs to be operated independently by the communities. From the summary of Table 3, we can conclude that the adsorption method is a good candidate for the technology implementation in rural areas because of the low cost and easy operation of the installation.

Biological methods

Biological processes -widely employed for H_2S removal, they are often economical and environmentally friendly. The use of chemotropic bacterial species (*Thiobacillus* genus), Microalgae cultures, anaerobic phototrophic bacteria (*Cholorobium limicola*) capable of oxidizing H_2S in the presence of light and CO_2.

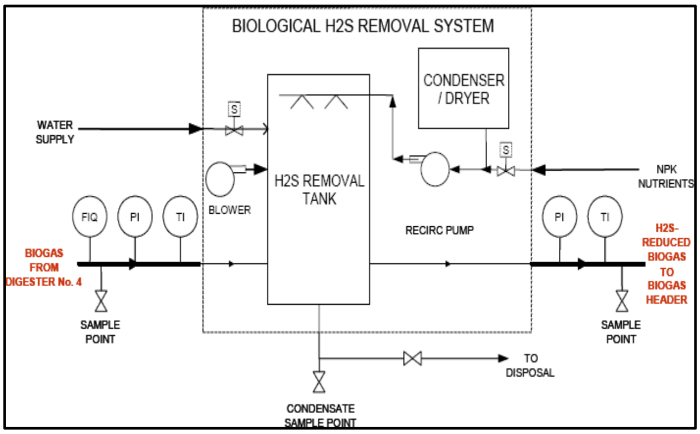

Fig 4: Biological Process for H_2S Removal

Compression

The energy density of upgraded biogas is comparatively low at ambient pressure and as a result it must be compressed at high pressures (e.g. 200-250 bar) to allow its sufficient storage in bottles/cylinders. Compressing biogas

- Reduces storage space requirements,
- Concentrates energy content and
- Increases pressure to the level needed to overcome resistance to gas flow.
- Compression can eliminate the mismatch of pressures and guarantee the efficient operation of the equipment.
- Biogas Compressors can be piston based, screw type, vane type, or liquid ring type compressors.

Biogas Bottling

Once the biogas is free from H_2S and CO_2, only methane gas is left as main constituent of biogas which is 'natural gas' for all practical purposes. This gas can be converted into CNG by multi-stage compression. Gas coming out of the scrubbing unit is at normal pressure, which is to be compressed 240 bar. Biogas, like Liquefied Petroleum Gas (LPG) cannot be converted into liquid state under normal temperature and pressure. It liquefies at a pressure of about 47.4 Kg/cm^2 at a critical temperature of -82.1^{0}C. Removing carbon dioxide, Hydrogen Sulphide, moisture and compressing it into cylinders makes it easily usable for transport applications as fuel for vehicles & also for stationary applications. Also, raw biogas can be compressed and bottled for remote applications of biogas. The compressed biogas can be used for injection into CNG Grid, Fuel for Vehicles, household and industrial application of biogas. It creates revenue when generated and sold for remote applications.

Table 4: Characteristic Comparison of Natural gas, Upgraded Biogas and Raw Biogas

Properties	Compressed Natural Gas	Upgraded Biogas	Raw Biogas
Composition % (v/v) Lower Heating Value	CH_4 – 89.14% CO_2 – 4.38% H_2 – .01% N_2 – .11% C_2H_6 – 4.05% C_3H_8 – 0.83% Iso-C_4H_{10} – 0.28% Neo-C_4H_{10} – 0.66% Iso-C_5H_{12} – 0.09% Neo-C_5H_{12} – 0.28% C_6H_{14} -0.17% 44.39 MJ/kg	CH_4 – 93% CO_2 – 4% H_2 – .06% N_2 – 2.94 % H_2S – 20 ppm 42.62 MJ/kg	CH_4 – 55-65% CO_2 – 35-45% H_2 – .02% N_2 – 1.98% H_2S – 500 ppm 20.5 MJ/kg
Relative Density	0.765	0.714	1.014
Flame speed (cm/sec)	34	–	25
Stoichiometric A/F (kg of Air/ kg of Fuel)	17.03	17.16	17.16
Auto-ignition Temperature (^{0}C)	540	–	650

Potential of CBG/Bio-CNG in India

Bio-CNG contains about 92-98 % of methane and only 2-8 % carbon dioxide. The calorific value of Bio-CNG is about 52,000 kilojoules (kJ) per kg, which is 167 % higher than that of biogas. The high methane content and calorific value combined with the low quantity of moisture, hydrogen sulphide and impurities make Bio-CNG an ideal fuel for automobiles and power generation. The low emission levels of Bio-CNG also make it a more environment-friendly fuel than biogas.

In India, Bio-CNG is estimated to replace two-thirds of India's Natural gas imports, which is currently at 429 billion cubic feet. In July 2016, the Waste to Energy Division of MNRE launched a programme on energy from urban, industrial and agricultural wastes/residues which aims to promote setting up of projects for recovery of energy in the form of biogas/Bio-CNG/enriched biogas from urban, industrial, and agricultural wastes. Central Financial Assistance (CFA) of INR 4 crore per 4800 kg of Bio-CNG/day generated from 12,000 cubic metre Biogas /day has been announced, with a limitation of Maximum CFA as INR 10 crore/project).

Presently, there are seventeen Bio-CNG plants operational in India, with a combined capacity of 46,178 kg per day. These plants are spread over nine states, of which Maharashtra leads in terms of the largest capacity as well as the highest number of plants. In addition, the National Agricultural Cooperative Marketing Federation of India is planning to develop a Bio-CNG facility near Azad Mandi in New Delhi.

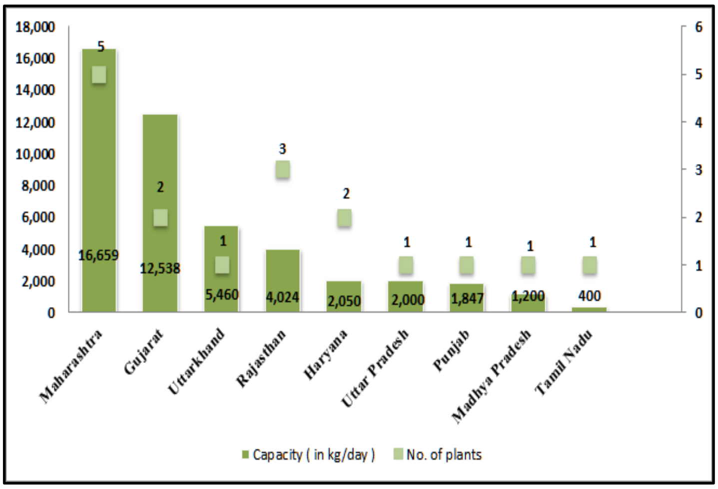

Fig 5: State-wise installed Bio-CNG capacity

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Table 3: Advantages and disadvantages of biogas purification methods

Methods	**Principles**	**Advantages**	**Disadvantages**
Water scrubbing	Separation based on solubility	➢ Methane recovery at 80–99% ➢ Methane loses 3–5% ➢ No chemical solvent ➢ Lower operational cost	➢ High energy consumption to regenerate solvent ➢ High water consumption ➢ Dissolved H_2S causes corrosion ➢ Clogging due to bacterial growth ➢ Corrosion
Chemical scrubbing	Separation based on solubility	➢ Methane recovery up to 95% ➢ Methane loses 0.1–0.2% ➢ Higher absorption capacity than *water scrubbing* ➢ Operational time is shorter than water scrubbing	➢ Energy intensive ➢ Corrosion ➢ Large amount of solvent ➢ Chemical waste may require treatment ➢ Solvent is expensive
Cryogenic Separation	Separation based on condensation temperature	➢ Methane recovery up to 98% ➢ Methane loses <1% ➢ Side product is pure carbon dioxide for *drying ice*	➢ High energy consumption ➢ Need more pre-treatment to remove H_2O and H_2S ➢ Uses lots of process equipment ➢ High operational and maintenance cost
Membrane technology	Separation based on molecule selectivity on membrane	➢ Methane recovery up to >96% ➢ Simple operation ➢ Low energy required ➢ Membrane is able to be generated	➢ Some membrane has low selectivity ➢ Often yields lower methane ➢ High-cost membrane
Adsorption	Separation based on the different selectivity of gases on adsorbent	➢ Methane recovery between 96 and 98% ➢ Methane loses at 2–4% ➢ Can use common and cheap adsorbent ➢ Simple installation and operation ➢ Adsorbent can be generated	➢ Some adsorbents are expensive, for example *metal organic materials* (MOMs) ➢ Methane loses in malfunctioning of valves

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