Strategic Technologies for Biogas Purification

Dr. M.J.Khalil, Kartik Sharma, and Rimzhim Gupta

Abstract—**The objective of this paper is to analyze the biogas production and biogas purification from anaerobic digestion, landfill wastes, animal sewage and waste-activated sludge consists primarily of CH_4, CO_2 and contaminants present in biogas are H_2S, siloxanesand water vapor. Various techniques have been developed to removal H_2S and CO_2 from a model landfill biogas. In adsorption process operates at near- ambient temperature and so differs from cryogenic distillation technique of gas separation and the high pressure separation process selectively separates H_2S and CO_2.**

However the maximum separation e.g. 99.99% is obtained by cryogenic technique.

Index Terms— **Biogas, Cryogenic separation, Pressure Swing Adsorption, biogas purification.**

I. INTRODUCTION

The development of biogas energy, which is considered as an important energy resources for future, is a fitting option to solve global environmental and energy issues in a sustainable manner. Biogas is produced by various sources, e.g. landfill sites, weeds, woods, grasses, leaves, fruits and vegetable solids wastes, wastewater treatments facilities, animal farm manure, algae, compost, sewage and agro-food sludge and even the organic fraction of municipal solid wastes (MSW) or is produced by anaerobic fermentation of manure.Typical biogas mainly consists of methane (50-70%) and carbon dioxide (25-45%), but it can also contain, depending on the source's composition, trace or significant quantities of undesirable contaminants, such as ammonia, hydrogen sulphide (0.005-2%), water (5-10%),siloxanes (0-0.2%), moisture, halogenated hydrocarbon (<6%), oxygen (0-1%), carbon monoxide (<6%)and nitrogen (0-2%). Nowadays several technologies such as cryogenic packed bed, biological processes, membrane separation, pressure swing adsorption, high pressure water scrubbing, physical or chemical absorption, anaerobic digestion and monofermentationtechnology are used to remove CO_2. However, these processes are expensive and can lead to high methane losses. Global warming or energy-related reduction of anthropogenic CO_2 emissions are increasing. Energy production accounts for about one- third of CO_2 emissions from fossil fuel use. Carbon dioxide capture and storage from flue gases a key measure to reduceCO_2emissions to the atmosphere. The purpose of CO_2 capture is to produce a concentrated stream that can be readily transported to a CO_2 storage site.

In this paper, various technologies mentioned have been removed hydrogen sulphide and carbon dioxide from biogas and this work describes of using a novel dynamically cryogenic packed-beds and compares it to other various technology (e.g. membrane, PSA and scrubbing) on the basis of product purity and energy requirements. Firstly, some details about the selected various technologies are shown in below. Finally, then the dynamically operated cryogenic packed-bed technique is described.

II. TECHNOLOGIES

A. *BIOLOGICAL PROCESSES.*

This technique is based on the principle of carbon dioxide removed from biogas revealed the existence of a linear relationship between the rate of cyanobacterium Arthrospira plantesis and carbon dioxide removed from biogas.

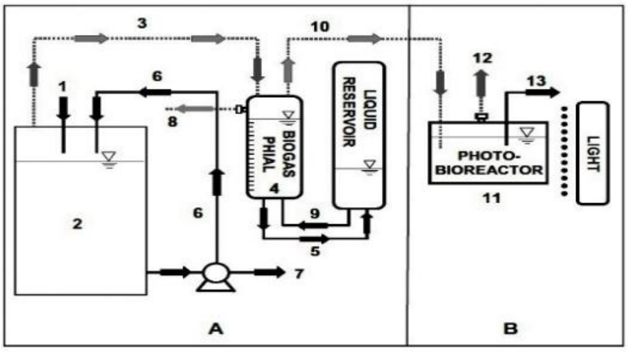

Fig.1. Diagram for (A) mixed sludge digestion and (B) CO_2 removal from biogas by cyanobacterium Arthrospira platensis photosynthetic. The overall process consisted of the following daily events: (1) fed batch pulse feeding of mixed sludge. (2) Anaerobic digestion in bench scale digester. (3) Biogas production in the digester. (4) Biogas accumulation in graduated phial. (5) Transfer of dilute H_2SO_4 solution from the phial to the reservoir to measure the biogas volume produced daily. (6) Recirculation of the digesting anaerobic sludge by peristaltic pump. (7)anaerobic sludge sampling. (8) biogas sampling. (9) displacement of dilute H_2SO_4 solution from the reservoir to the phial. (10) resulting transfer of biogas accumulated daily in the phial to the photobioreactor. (11) A. platensis photoautotrophic growth. (12) sampling of O_2 enriched biogas after photosynthetic treatment. (13) sampling of A. platensis suspension. Continuous lines refer to liquid phase flows and whereas dotted lines to gas phase flows.

A schematic diagram of the experimental setup used for the sludge anaerobic digestion and biogas purification is shown in the Fig.1. It has two components connected in series: first section are mixed sludge anaerobic digester for the biogas production and second section are a glass vessel for carbon

Dr. M.J.Khali, Department of Chemical Engineering, Aligarh Muslim University, Aligarh-202002, INDIA
Kartik Sharma, Department of Chemical Engineering, Aligarh Muslim University, Aligarh-202002, INDIA
Rimzhim Gupta, Department of Chemical Engineering, Aligarh Muslim University, Aligarh-202002, INDIA

dioxide removed from biogas by the use of photosynthetic growth of the cyanobacterium Arthrospira plantesis. The mixed sludge found from waste and wastewater treatments plants was daily fed and according to the fed-batch pulse feedingsystem of mode of operation. The anaerobic digestion in batch scale placed in the thermostatted water bath and the reactor with the sludge from a full- scale digester, the mixed sludge was daily fed. The transfer of dilute H_2SO_4 solution from the phial to the reservoir to measure the biogas volume produced daily. The digesting anaerobic sludge was time to time running continuously re-circulated by a peristaltic pump and sample were collected from a sampling section point and situated in the upper part of the digester, in which the produced biogas was collected and so displacement of a dilute H_2SO_4 acid solution colored with methyl range from the reservoir to the phial. The resulting transfer of biogas accumulated daily in the phial (liquid level displacement) to the photobioreactor and avoid any contact with outside air. Anthrospira platensis was cultivated in closed condition for the gas phase using biogas CO_2 as a carbon source.

B. PRESSURE SWING ADSORPTION.

Adsorption technology (Fig.2.) is used for separation process. Separation of $CO_2$from gas (CO_2/CH_4) mixtures by adsorption is based on differences in equilibrium capacities of adsorbent surface (example zeolites, carbon molecular sieves). A gas (CO_2/CH_4)mixture was used as a feed gas components.

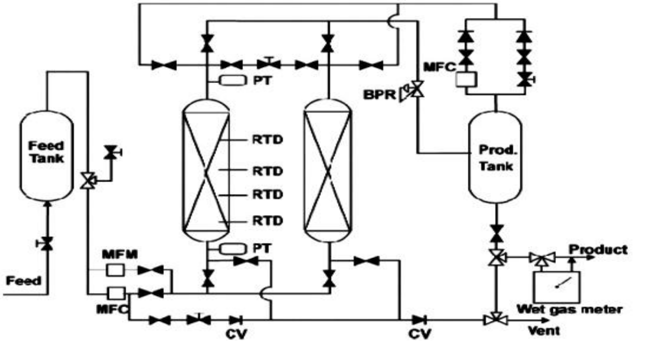

Fig.2. Schematic diagram of apparatus for a two-bed PSA process: (MFC) mass flow controller; (MFM) mass flow meter; (PT) pressure transducer; (BPR) back-pressure regulator; (RTD) resistance temperature detector; (CV) check valve.

In this two-bed pressure swing adsorption process, the desired product is CH_4 (raffinate). This experiments was performed by Skarstron cycle with concurrent pressure equalization. This simple six steps two bed PSA (1) pressurization of feed gas (2) high pressure adsorption (3) depressurizing pressure equalization (4) counter-current depressurization (5) purge with light (6) pressurizing pressure equalization. During 3 step which is pressure equalization for conservation of energy and separative work, high and low pressure beds are connected through the product ends. To obtain purified biogas various contaminants (like sulphure and other halogenated compound) must be removed for this adsorbent testing is done, identify the component which can remove these contaminants.

Mathematical model:

The component and overall mass balances for the bulk phase:

$$-D_L \frac{\partial}{\partial z}\left(C \frac{\partial \left(\frac{c_i}{C}\right)}{\partial z}\right) + \frac{\partial (u c_i)}{\partial z} + \frac{\partial c_i}{\partial t} + \rho_p \left(\frac{1-\epsilon}{\epsilon}\right) \frac{\partial q_i}{\partial t} = 0$$

$$-D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial (uC)}{\partial z} + \frac{\partial C}{\partial t} + \rho_p \left(\frac{1-\epsilon}{\epsilon}\right) \sum_{i=1}^{n} \frac{\partial q_i}{\partial t} = 0$$

The energy balance for the gas phase:

$$-K_L \frac{\partial^2 T}{\partial z^2} + \epsilon \rho_g C_{pg} u \frac{\partial T}{\partial z} + \left(\epsilon_t \rho_g C_{vg} + \rho_B C_{ps}\right) \frac{\partial T}{\partial t} - \epsilon_t RT \frac{\partial C}{\partial t} - \rho_B \sum_{i=1}^{n} (-\Delta H_i) \frac{\partial q_i}{\partial t} + \frac{2h_i}{R_{B_i}} (T - T_w) = 0$$

Another energy balance for the wall of the adsorption:

$$\rho_w C_{pw} A_w \frac{\partial T_w}{\partial t} = 2\pi R_{B_i} h_i (T - T_w) - 2\pi R_{B_0} h_0 (T_w - T_{atm})$$

C. MEMBRANE PURIFICATION.

The schematic flow diagram of the reactor is given in Fig.3.

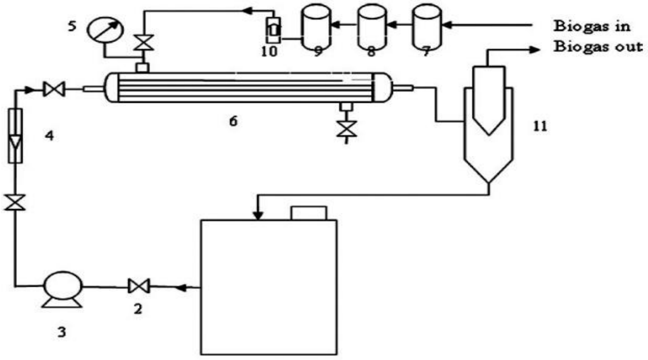

Fig.3.The process flow diagram of the reactor for biogas purification. (1. Bin, 2.Flange, 3. Liquid pump, 4. Fluid flowmeter, 5.Pressure gauge, 6. Membranous reactor, 7. Dehydrating tower, 8. Desulfurizing tower, 9.Gasholder, 10. Gas flowmeter, 11. Liquid−gas separator).

The biogas was purified in the membrane reactor and biogas was fed from the upper of the column and the $Ca(OH)_2$was fed from the left margin of column. The membranous reactor contained seven membranous tubes. Biogas entered each membranous tube through pores, was in the form of very small bubbles under the external pressure. After the reaction between $Ca(OH)_2$ and CO_2 suspension, CH_4 was separated from mixture of liquid and gas as it flowed through the liquid-gas separator. The CO_2concentration in the biogas entering and leaving the column were constantly monitored by a gas chromatograph.

D. CRYOGENIC PACKED PED.

The CPB concept (fig.4&5.) has been extensively developed to capture $CO_2$from flue gas and biogas treatment.

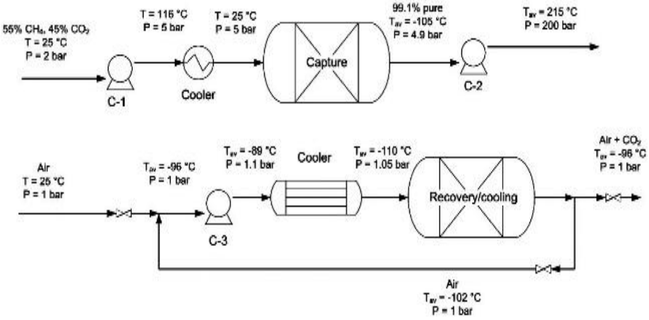

Fig.4. Simplified process scheme including conditions for the base case.

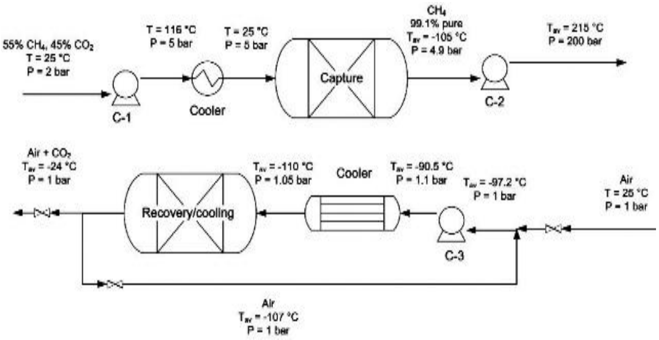

Fig.5. Simplified process scheme including conditions and recovery/cooling step in reversed flow mode.

The CPB process based on dynamic operation of packed bed, which are operated in cooling, capture and recovery step. The bed is cooled down to a temperature low near -100°C& high pressure almost 40 bars enough to condensate/ desublimate the contaminants (e.g. CO_2, H_2O) and remain gaseous (e.g. CH_4 or N_2). A condensate CO_2will move toward outlet of the bed and gaseous $CO_2$is fed to the bed in order to obtain pure CO_2 .Finally, the distillation column separates CH_4 from the other contaminants, mainly CO_2&H_2S.

Fig.6.CO_2ice formed at the packing surface during a capture cycle.

III. MODEL EQUATIONS FOR THE 1-D PSEUDO-HOMOGENEOUS MODEL:

Component mass balance for the gas phase:

$$\varepsilon_g \rho_g \frac{\partial \omega_{i,g}}{\partial t} = -v_g \rho_g \frac{\partial \omega_{i,g}}{\partial z} + \frac{\partial}{\partial z}\left(\rho_g D_{eff} \frac{\partial \omega_{i,g}}{\partial z}\right) - \dot{m}_i a_s + \omega_{i,g} \sum_{i=1}^{n_c} \dot{m}_i a_s$$

Component mass balance for gas phase:

$$\frac{\partial m_i}{\partial t} = \dot{m}_i a_s$$

Total continuity equation for the gas phase:

$$\frac{\partial(\varepsilon_g \rho_g)}{\partial t} = -\frac{\partial(v_g \rho_g)}{\partial z} - \sum_{i=1}^{n_c} \dot{m}_i a_s$$

Energy balance (gas and solid phase):

$$(\varepsilon_g \rho_g C_{p,g} + \rho_s (1-\varepsilon_g) C_{p,s}) \frac{\partial T}{\partial t} = -\rho_g v_g C_{p,g} \frac{\partial T}{\partial z} + \frac{\partial}{\partial z}\left(\lambda_{eff} \frac{\partial T}{\partial z}\right) - \sum_{i=1}^{n_c} \dot{m}_i a_s \Delta h_i$$

A. SCRUBBING.

The scrubbing concept (Fig.7.) has been extensively developed to remove $CO_2$and H_2S from water and other is polyethylene glycol & a physical and chemical solvent.

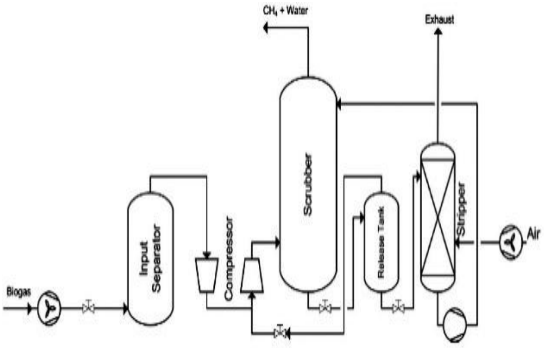

Fig.7. Schematic diagram of water& PEG scrubbing.

The process is based on the absorption process, which are purely physical. Usually biogas is pressurized and fed to the bottom of a packed column while water is fed on the top and so absorption process is operated counter-currently. Water scrubbing can be used for selective removal of H_2S since H_2S is more soluble than CO_2 in water. Water which exits the column with absorbed $CO_2$and/or H_2Scan be regenerated and re-circulated back to the scrubber.

A. PHYSICAL OR CHEMICAL ABSORPTION.

This technology is used for the removal of $CO_2$and H_2S from gas mixture & biogas treatment. It is ability to operate at low pressure.Chemical absorption (Fig.8.) involves formation of reversible chemical bonds between the solute and the solvent.

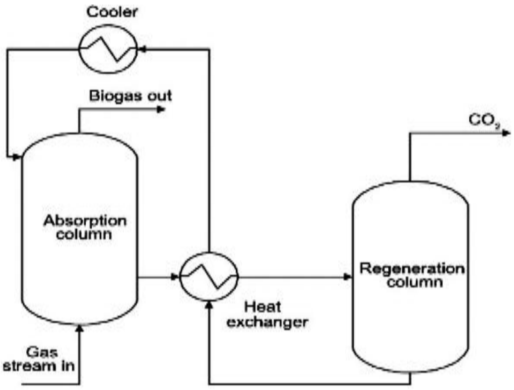

Fig.8. Schematic diagram of chemical absorption.

In the case of CO_2absorption, the following reactions take place:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$
$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$$
$$CO_2 + RNH_2 + H_2O \rightarrow RNH_3^- + HCO_3^-$$
$$CO_2 + RR'NH \rightarrow RR'NCOO^- + H^-$$

Regeneration of the solvent, therefore, involves breaking of these bonds and correspondingly, a relatively high energy input.Chemical solvents generally employ either aqueous solutions of amines or aqueous solution of alkaline salts.

B. ANAEROBIC DIGESTION.

In this technology, sludge was obtained from waste and wastewater treatment plant. A mineral salt medium was used in the characterization of CO_2 mass transfer in the absorption columns.

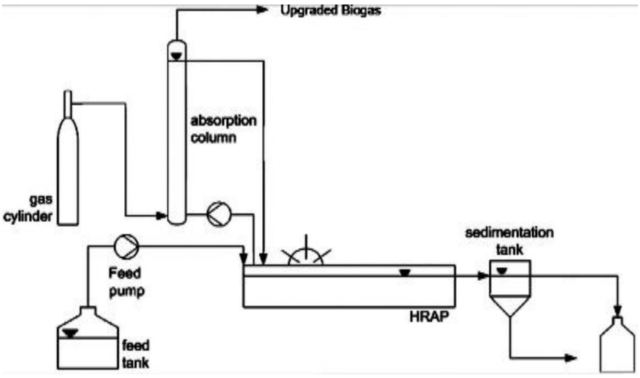

Fig.9. Schematic diagram of the continuous biogas upgrading.

The high rate algal pond (HRAP) interconnected via liquid recirculation with an external absorption column for the removal of $H_2O\ and\ CO_2$ from biogas using an alkaliphilic micro algal-bacterial consortium and the removed 100% of the $H_2O$and 90%of the CO_2supplied with O_2 concentrations in the upgraded biomass below 0.2%. Finally, the production of methane from the inoculum to obtain the net methane production from the algal-bacterial biomass generated in the biogas upgrading process.

IV. DISCUSSION AND CONCLUSION

A novel process for biogas treatment using various technique has been proposed. The method was employed to purify biogas and different chemical addition showed negligible effects on the biogas purification efficiency. The rate of biogas purification was all greater than 99.0% in different condition. The cryogenic separation concept shows to be favorable when compared to PSA technology. The purity and recovery of the obtained $CH_4$are greater than in PSA and purity is 99.99% possible at lower temperature.

To select an appropriate technique for H_2Sremoval, the technique to remove CO_2 should be considered firstly. A technique such as absorption in water or selexol, membrane or PSA/VPSA that removes H_2S as well as $CO_2\ and\ H_2S$ is present in high concentration CO_2removal technique such as absorption with amines.

Each of the mentioned technologies in this work, except the biological, cryogenic separation, anaerobic digestion technique, is in operation in large scale. Moreover, a technology can also be chosen according to the highest achievable methane concept. Water scrubber technology are used mostly. This study focused on the CH_4/CO_2separation and showed the possibility to removed H_2S.

V. NOTATION

α_s =specific solid surface area per unit bed volume, $\frac{m^2}{m^3}$.
C_p = heat capacity, J/Kg K
D_{eff} = = effective diffusion coefficient, m^2/s
$D_{h,c}$ =hydraulic diameter of the monolithic channels, m
f= fanning friction factor for the monolithic channels.
L= bed length, m
m_i =mass deposition of component i per unit bed volume, kg/m^3
$\dot{m}_i$ =massdeposition rate per unit surface area for componenti, $kg/m^2\ s$
n_c = number of components
p = pressure, Pa
Re = Reynolds number
t = time, s
T = temperature, K, ℃
v = superficial velocity, m/s
z = axial coordinate, m

Greek Letters

Δh_i = enthalpy change related to the phase change of component i, J/kg
ε_g= bed void fraction
η = viscosity, kg/m/s
λ_{eff} =effective conductivity, W/mK
ρ = density, kg/m^3
ω = mass fraction, kg/kg

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REFERENCES

[1]Elisabetta Finocchio, Tania Montanari, Gilberto Garuti, Chiara Pistarino, Flavio Federici, Michela Cugino, and Guido Busca, *"Purification of biomases from siloxanes by adsorption: On the regererability of activated carbon sorbents"*, Energy & Fuels 2009, 23, 4156-4159.
[2] Ralf Schmersahl, Jan Mumme, and VolkhardScholz, *"Farm-based biogas production, processing, and Use in polymer electrolyte membrane (PEM) fuel cells"*, Ind. Eng. Chem. Res. 2007, 46, 8946-8950.
[3] Melanie Bahr, Ignacio Diaz, Antonio Dominguez, Armando Gonzalez Sanchez, and Raul Munoz, *"Microalgal-Biotechnology as a platform for an integral biogas upgrading and nutrient removal from anaerobic effluents"*, Environ. Sci. Technol. 2014, 48, 573-581.
[4] Xiujin Li, Laiqing Li, MingxiaZheng, Guozhi Fu, and Jam SaifullahLar, *"Anaerobic co-digestion of cattle manure with corn stoverpretreated by sodiumhydroxide for efficient biogas production"*, Energy Fuels 2009, 23, 4635-4639.
[5] E. Ryckebosch, M. Drouillon, H. Vervaeren,*"Techniques for transformation of biogas to biomethane"*,Biomass and Bioenergy 2011, 35, 1633-1645.
[6] Min-Bae Kim, Youn-Sang Bae, Dae-Ki Choi,and Chang-Ha Lee, *"Kinetic separation of landfill gas by a two-bed pressure swing adsorption process packed with carbon molecular sieve: nonisothermal operation"*, Ind. Eng. Chem. Res. 2006, 45, 5050-5058.
[7] A. Converti, R.P.S. Oliveira, B.R. Torres, A. Lodi, M. Zilli, *"Biogas production and valorisation by means of a two-step biological process"*,Bioresource Technology 2009, 100, 5771–5776.
[8] N. Tippayawong, P. Thanompongchart, *"Biogas quality upgrade by simultaneous removal of* CO_2*and* H_2S *in a packedcolumn reactor"*, Energy 2010, 35, 4531-4535.
[9] Martin J. Tuinier and Martin van SintAnnaland, *"Biogas purification using cryogenic packed-bed technology"*,Ind. Eng. Chem. Res. 2012, 51, 5552−5558.
[10] Jun Zhou, Xun Cao, Xiao-yu Yong, Shu-ya Wang, Xi Liu, Yi-lu Chen, Tao Zheng,and Ping-kai Ouyang, *"Effects of various factors on biogas purification and nano-CaCO$_3$ synthesis in a membrane reactor"*, Ind. Eng. Chem. Res. 2014, 53, 1702−1706.
[11] M.J. Tuinier, M.vanSintAnnaland, G.J.Kramer, J.A.M.Kuipers, *"Cryogenic CO$_2$ capture using dynamically operatedpackedbeds"*,Chemical Engineering Science 2010, 65, 114 -119.