Design and Analysis of Packed Bed Activated Carbon Reactor for the Enrichment of Biogas

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Abstract- Biogas produced by anaerobic digestion of organic matters has reasonable potential to replace natural gas need of the world energy consumption. According to the UK National Non-Food Crops Centre (NNFCC), the anaerobic digestion (AD) industry experienced rapid growth in recent years. Thus, there is an increasing demand for the enriched biogas, to be used as vehicle fuel or injected to the natural gas grid. Since a typical biogas contains 50-65% methane, 30-45% carbon dioxide, 1000 - 10,000 ppm hydrogen sulphide, the removal of carbon di-oxide and hydrogen sulphide is required for upgrading the biogas. A number of methods exist for enriching biogas including water scrubbing system, membrane separation, chemical absorption, cryogenic separation and physical adsorption. Among these methods, adsorption by activated carbons (AC) is considered as an efficient and economical approach. The uniqueness of the activated carbon as adsorbents is due to their high surface area, developed pore volume and surface properties. Accordingly, this research has been focused on adsorption of activated carbon. An activated carbon packed-bed reactor designed and commissioned at laboratory scale. Biogas mixture passed through the packed bed reactor and benchmarked against the Standard Industrial Activated Carbon (SIAC). Break through curves were used to assess the adsorption capacities. It is envisioned that this method can transform the enrichment of bio-gas for power generation systems. The results obtained from the current research could be utilized as a guide for the further design and operation of the industrial system.

Keywords- Biogas, Packed Bed Reactor, Physical Adsorption, Standard Industrial Activated Carbon.

I. INTRODUCTION

AD is the biological treatment of biodegradable organic waste in the absence of oxygen, utilizing microbial activity to break down the waste in a controlled environment [i]. The AD of organic material basically takes place in four steps, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis as shown in Fig. 1 [ii].

There is an increasing local interest in the use of biogas as an alternative to fossil fuels, and hence, there has been a steady increase in the renewable power derived from anaerobic digestion system.

An exponential growth in the world's population and rapid economic development has led to a tremendous demand for energy [iii-vii]. Fossil fuels are currently the main energy source for this global energy demand [viii-ix]. However, the reserves of fossil fuels are limited and often placed in geo-political challenged locations [x-xi]. Also negative environmental effects of using fossil fuels include acid rain, ozone layer depletion and global climate change [xii-xvi]. The result has been a rapid growth in the level of greenhouse gas emissions and an increase in fuel prices, which are the main driving forces behind efforts to utilise renewable energy sources [xvii-xviii].

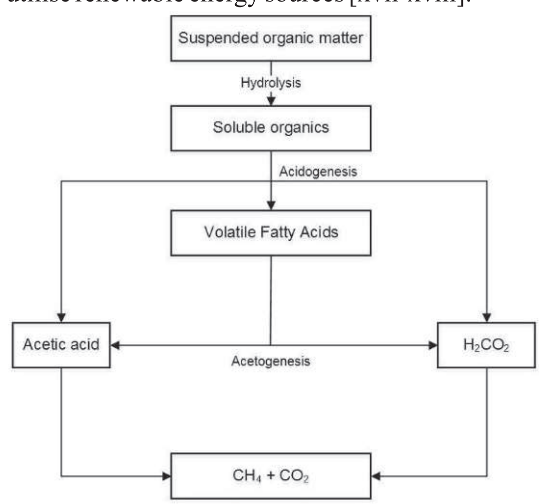

Fig. 1. Steps in the anaerobic digestion process [xix]

Biogas usually refers to a gas formed by the biological breakdown of organic matter in the absence of oxygen. Biogas derives from biogenic material, biofuels type. Biogas is produced through anaerobic digestion or fermentation of biodegradable materials which includes biomass, sewage, manure, municipal waste, green waste, and plant material and energy crops. This type of biogas comprises primarily methane and carbon dioxide. Also the gas produced by the use of biomass which is wood gas created by gasification of wood or other biomass. This type of gas consists primarily of nitrogen, hydrogen, and carbon monoxide, with trace amounts of methane.A typical biogas composition is shown in Table I.

TABLE I
TYPICAL BIOGAS COMPOSITION [xx]

Content	Composition
Methane	50-60 %
Carbon Dioxide	30-45 %
Hydrogen Sulphide	1000-10,000 ppm
Hydrogen	0-1 %
Oxygen	0-2%

Agricultural organic streams include manure and slurries of different animals, energy and crops. Industrial organic waste streams includes by-products from food processing such as milk and cheese manufacture, slaughter houses and vegetable canning, from the beverage industry, such as fruit processing, distilleries, coffee, soft drinks, and from industries, including paper and board, sugar plants, rubber and pharmaceuticals. Municipal solid waste contain organic fraction of household waste. Methane content is 50-60% on average but its percentage is higher for the waste from agro food industry. The CO_2 is 30-45 % on average from all sources. The H_2S concentration varies with the different sources, but it is higher for sewerage, agriculture and animal waste from 600 ppm to 20,000 ppm average, as compared to municipal and landfill, where the concentration of H_2S varies from 3 ppm to 3000 ppm. Most intended uses of H_2S have considerable lower threshold for H_2S content and removal of H_2S is thus required to ensure the H_2S content is below the allowed amount.

Hence, there is a strong political drive towards the enrichment of biogas, since its properties are comparable to natural gas. Hence it could be used as a fuel for the same applications as fossil natural gas [xxi].

A range of techniques are available for the up gradation of biogas into bio-methane. Fig. 2 lists these techniques. Several processes are available in the literature for the upgrading the biogas into bio-methane, including high pressure water scrubbing, chemical absorption, cryogenic separation, membrane separation, and physical adsorption. High pressure water scrubbing is currently the most commonly used, since gases dissolves into the water while CH_4 does not because of their difference in solubility.

Physical absorption technique used the water with high pressure as absorber. The unrefined biogas supplied in a packed column from down side & the water with high pressure sprayed from the top side of the column reactor. Hence this process becomes with the counter current flow direction. The unwanted components of biogas i.e. carbon dioxide & hydrogen sulphide separated from the gas on the basis of the solubility in the water. These gases separated at the bottom of the column [xxii]. Chemical absorption involves formation of reversible chemical bonds between the solute and the solvent. 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, i.e. mono-, di- or tri-ethanolamine or aqueous solution of alkaline salts, i.e. sodium, potassium and calcium hydroxides. [xxiii]. Membrane separation technique is another possible method for the biogas up gradation. With the help of a thin membrane some gas elements from the unrefined biogas could be transported. Normally the elements with less than 1 mm thickness separated by the membrane, while the other keep hold as it is. Due to the difference in the partial pressure the respective components are transported through the membrane, which is depending upon the component's permeability in the membrane. Permeability should be higher to get the high methane transparency [xxiv]. This process undergoes with a pressure of 25-35 bar and normally the solid membranes are used for this purpose. These membranes are of acetate cellulose materials which has the permeability with higher values. . This method is not suitable for high purity needs Consumes relative more electricity per unit of gas produced [xxv].The cryogenic method of purification involves the separation of the gas mixtures by fractional condensations and distillations at low temperatures. The process has the advantage that it allows recovery of pure component in the form of a liquid, which can be transported conveniently.

However, attempts to apply the cryogenic process for the removal of CO_2 from digester gas by Los Angeles County sanitation have not proven successful. Rather complicated flow streams are involved and thermal efficiency is low. Capital cost high Requirement of large sites. Longer start-up and shut down process Limited scalability in production. Capital cost and utility requirements are also high [xxvi].

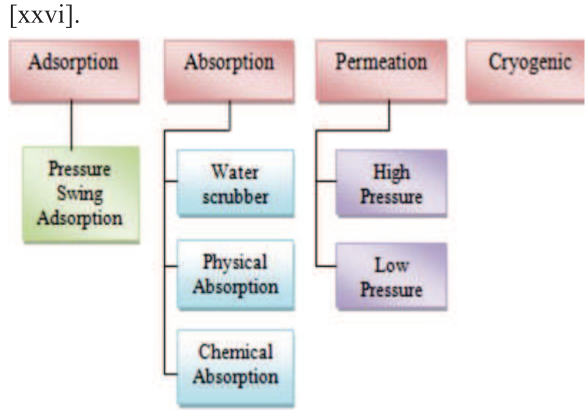

Fig. 2. Biogas upgrading technologies options [xxii]

However activated carbon adsorption is the most efficient method for enriching biogas system. Hence, the aim of this research is to establish an effective method for up-grading by physical adsorption of activated carbon.

II. Experimental

A. Materials and Methods

A packed bed activated carbon reactor installed and commissioned for the adsorption analysis of activated carbonfor biogas enchainment process. Adsorption unit made of stainless-steel tube (25mm OD, 290mm length). Different samples of standard industrial activated carbon were used as adsorption material of the packed bed reactor. Samples were given names as C-1, C-2 and C-3 respectively. All the samples of activated carbon were selected with different physical structure. The sample C-1 is granular and it is produced by steam activation at high temperature using a propriety process, which does not involve the use of any impregnant. C-2 has a structure of pallets. It is developed for the purification process from air streams and eliminating odours. It is the cost effective solution for the removal of "nuisance" type odours. As a result the risk of bed fires due to exothermic reactions is greatly reduced. C-3 is the powdered activated carbon. A powdered activated carbon with high adsorptive capacity, good filterability, and above average purity that is particularly suited for many purification applications.Glass wool was used at the bottom end of the rig to prevent the activated carbon to fall into the tube below. Similarly, a filter paper was used on the top side for smooth flow of the gas. Methane and carbon dioxide gases were used from the gas lines in the laboratory where as a special gas cylinder (BOC Ltd) was used with 1%H_2S/ 99%N_2. Physical adsorption method was used for the adsorption analysis at different flow rates.

TABLE II
SPECIAL GAS CYLINDER SPECIFICATIONS

Gas Mixture:	1% Hydrogen Sulphide/Nitrogen
Material number:	151885-AV -C
Cylinder size:	AV* (680mm x 181mm - 10 liquid litre capacity)
Pressure (bar):	200
Contents:	1.9m^3
Valve outlet:	BS15
Shelf-life:	36 months

B. Experimental Set-up of Packed-bed Reactor

A packed bed reactor of activated carbon was used for the present research. Different gas mixture were used for the biogas as shown in Fig. 3. Methane and carbon di-oxide gases from the gas lines while a cylinder of special gas mixture of $H_2S/N_2$was used. This cylinder consist of 1% hydrogen sulphide with 99% mixture of nitrogen gas. The properties of the special gas mixture has been shown in Table II. Pressure regulators andflow meters were used for controlling the pressure and volume flow of the gas in the reactor. Pressure regulators were fixed with the gas lines whereas flowmeters (Omega Ltd. UK) were installed with the rig at the time of assembling the unit. A safety valve was mounted with adsorption unit and the rig was placed inside the fume-hood for the safety reasons. A mass-spectrometer (Hiden Analytical Ltd. UK) is attached at the exit side of the rig, which is used to analyse the gases. Mass-spectrometer was further attached with the mass-soft to quantify the adsorption amount.

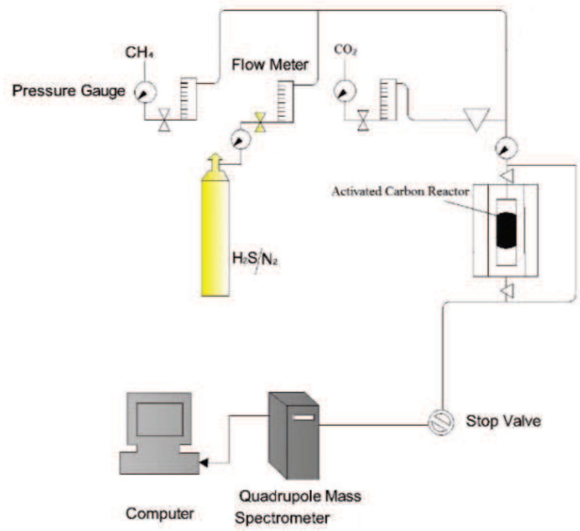

Fig. 3. Experimental set-up of the adsorption unit

C. Activated Carbon Characterization

CHN (Carbon, Hydrogen & Nitrogen) analyses were conducted on 440 Elemental Analyser (Control Equipment Cooperation). Isotherms of nitrogen were taken using Micrometrics Gemini VII. The catalyst degassed at temperature of 200°C for half a day with nitrogen gas by using Micrometrics Flow prep 060. Specific surface area is one of the imperative properties which affect the adsorption capacity of activated carbon significantly. Different surface areas for all the samples were measured and shown in Table IV below.

III. Overview of the Process Analyses

In the present study, biogas enrichment was carried with the physical adsorption system. Activated carbon material was selected for this purpose and different analyses were conducted for finding the adsorption capacities of activated carbon samples. These analyses includes surface area, elemental and adsorption analyses. Risk assessment was prepared before the analyses to determine the process viability of the adsorption system. This includes COSHH (Control of Substances Hazardous to Health) and MSDS (Material safety Data Sheets) provided by the manufacturer for all the materials used. Leak test was conducted every time before filling the new sample in the reactor. Breakthrough curves were used for the adsorption capacities of the process.

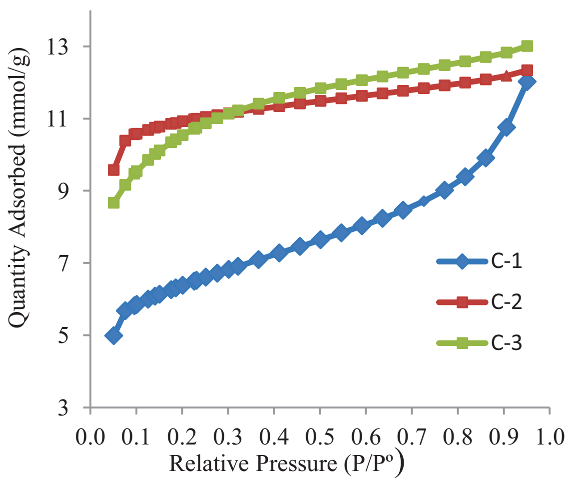

Fig. 4. Overview of the process analysis

IV. Results and Discussions

A. Elemental Analysis

CHN analyses were conducted on 440 Elemental Analyser (Control Equipment Cooperation). In the analyser carbon, hydrogen and nitrogen content in organic and inorganic compounds can be determined. Combustion of the samples occurs in pure oxygen under static conditions. Helium was used to carry the combustion products through the analytical system to atmosphere because it is chemically inert relative to tube packing chemicals, and it has high co-efficient of thermal conductivity. The percentage of carbon, nitrogen and hydrogen obtained from elemental analysis for all samples of activated carbon is given in Table III.

TABLE III
ELEMENTAL ANALYSIS OF AC SAMPLES

Sample	% C	% H	% N
C-1	76.21	0.59	0.3
C-2	82.25	0.13	0.37
C-3	81.38	0.2	0.11

B. Surface Area Analysis

Nitrogen isotherms were used to calculate the specific surface area, micro-pore volume, and total pore volume. All parameters and pore size distributions were calculated using the Density Functional Theory (DFT) [xxv]. The surface area was calculated using the BET method. The internal surface area of the activated carbon is usually determined by BET method (Brunaurer, Emmett and Teller). This method utilizes the low pressure range of the adsorption isotherms of a substance of known dimension which is usually nitrogen. This region of isotherms is generally distributed to monolayer adsorption. Hence, by considering the material is only adsorb one molecule deep on the surface of the carbon, the surface area can then be measured by using the following equation

$S = X_m NA$

S = Specific surface in m2/g

X_m = sorption value (ratio of the weight of the nitrogen adsorbed and carbon sample)

N = Avagardo's number, 6.025 E+23

M = Molecular weight of the nitrogen

A graph of adsorbed quantity for different activated carbon samples is shown in Fig. 4. Figure shows the quantity of the different activated carbons absorb with respect to the relative pressure. C-1 found with the linear increase of pressure. C-2 and C-3 absorption gives the smooth curves for the adsorption for the relative pressure values.

Table IV shows surface areas of activated carbon samples used for the analysis. There are normally four different type of surface area are used. These includes Single point, BET, Langmuir and t-Plot External Surface Area. However, BET surface adsorption theory is based on multilayer adsorption which addressed some flaws in Langmuir theory which is monolayer adsorption.

TABLE IV
BET ANALYSIS OF ACTIVATED CARBON SAMPLES

Samples	Single Point Surface Area	BET Surface Area	Langmuir Surface Area	t-Plot External Surface Area
	m^2/g	m^2/g	m^2/g	m^2/g
C-1	0.301107	202.8039	839.1614	258.1577
C-2	0.301109	265.6395	1,200.3939	153.8693
C-3	0.301257	277.6921	1,239.4617	443.3491

C. Adsorption Capacity of Activated Carbons

Adsorption capacities of all the activated carbon samples were calculated at different temperatures ranges from 25°C to 75°C as shown in Fig. 5. Each sample of activated carbon was chosen with different physical structure. C-1 is small grains physical appearance, C-2 in pallet form whereas C-3 is in powder form. These capacities of samples were calculated on the basis of the material quantitative analysis. It can be seen that at 25°C, C-1 &C-2 has good adsorption capacity of about 50-60% compared to C-3, 38%.However, C-2 seems to have good adsorption capacity than the other samples at 50°C.

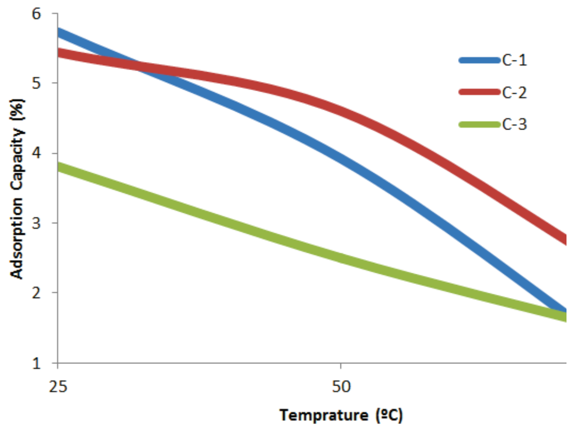

Fig. 5. Adsorption capacities of activated carbons at different temperatures

Anaerobic digestion takes place in the thermophilic region where digestion occurs at higher temperatures between 50 and 57 °C which is suitable for thermophilic bacteria. However, C-2 has comparatively high adsorption rate than the other two samples used for the analysis.

Thus, temperature range 50 to 60 °C are the best described for adsorption capacities of the activated carbon for the anaerobic digestion process. On the contrary, capacities of all activated carbon samples at 75°C are very small.

V. Conclusions

In the present energy crisis, biogas utilization after enrichment can be one of the most affordable methods for renewable power generation applications and home heating. Different technologies for the biogas clean-up technologies were studied. A number of methods are available for the upgradation of the biogas. However, there is need to find a potential solution for upgrading the gas which are environmental friendly. The present research was focused to find out the efficient way for the biogas purification system by activated carbon adsorption. The uniqueness of activated carbons as sorbents is related to their high surface area, high pore volume, and hydrophobicity of the surface.

In the present research, different gas mixtures passed through the packed bed activated carbon reactor. Measurements of the gases before and after treatment with the adsorption reactor were taken. Reduction of the carbon dioxide was observed from the mass spectrometer, which is coupled with the computer system through software. Results were analysed withadsorption curve with different activated carbon samples as explained in the results section. Hence, the results obtained from the current research could be utilized as a guide for the further design and operation of the industrial system.

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