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Optimization of an organic waste biogas reactor

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Pakistan is a country that has the potential to compete with any country in the world, but due to some reasons it is not able to utilize its full potential. One of the reasons for its slow progress is the shortage of energy. This problem can be reduced to a certain extent by utilizing the resources that are available in Pakistan that is moving towards renewable sources of energy such as biofuels. The production of biogas from organic waste can be done in many ways, but the most efficient and applicable process is the production of biogas through anaerobic treatment of organic waste. Pakistan has livestock of around 56.9 million of cows, buffalos and bullocks. The animal dung produced is around 854 million per day. If half of this quantity is used for biogas production almost 21.35 million m^3 of biogas can be produced, which also means that 450 million tons of biofertilizer are also produced per day. Dung containing bedding can produce about 100 m^3 of biogas from 1 ton. Also, 5700 GWh of electricity can be annually produced from bagasse (the fibrous residue of sugarcane after its processing). The scope of this study is to convert organic waste into biogas. Biogas can be used as domestic and vehicle fuel. The results obtained in bioreactors with and without agitation is that gas is produced in both cases but the time required to produce is different, in 15 days with continuous agitation and in 25 days without agitation.

Keywords: Biogas; Organic waste; Aerobic digestion; Anaerobic digestion; Bioreactor; Agitation.

INTRODUCTION

Generating and using a sustainable power source, both in a worldwide and a national setting are required by the impact of environmental change and consistent value ascent of fossil fuels. The primary explanations behind the spread of sustainable power sources are to expand the security of the energy supply and to acknowledge add up to energy autonomy. So, as to save the decreasing reserves of fossil fuel based energy sources and to end the environmental change, it is important to change the renewable energy sources and their utilization step by step over the next coming years. Renewable sources of energy offer the highest preservation and advancement choice for the future at affordable prices; many developed, as well as underdeveloped countries working on the use of biogas [1, 2].

Biogas is formed by the decomposition of organic matter in the absence of oxygen. Biogas is a clean and renewable fuel which can be harnessed by man. It can be produced from raw materials like agricultural waste, kitchen waste, human waste, plant waste or sewage. Biogas comprises mainly methane (the cause of energy inside the fuel) and carbon dioxide, as appears in Figure 1. It may also contain hydrogen or nitrogen in little amounts. Contaminants in the biogas can incorporate sulfur or siloxanes [3, 4].

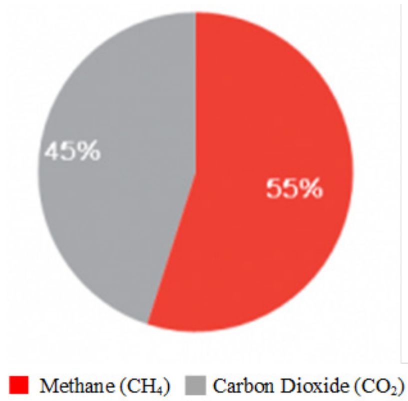

Fig. 1. Biogas composition from agricultural residue

The contents of methane and carbon dioxide in the biogas are impacted by various aspects including the proportion of starches, proteins, fats in the feedstock and the weakening element in the digester. The produced biogas can supplant conventional energy sources like firewood and animal dung, in this manner adding to battle deforestation and soil exhaustion. Biogas can add to supplant petroleum products, in this manner dwindling the emanation of ozone-harming substances and other destructive outflows, and changing natural waste into high-quality fertilizer [4, 5].

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Different components impacting achievement have been nearby natural directions and different strategies overseeing land use and waste transfer. In light of these ecological weights, numerous countries have executed or are thinking about strategies to lessen the natural effects of waste transfer. Many countries utilize anaerobic absorption as a pretreatment step that brings down slop transfer costs, controls scents, and decreases the expenses of conclusive treatment. Pakistan produces almost 1 billion tons of animal waste and 225000 tons of agricultural waste. Our goal is to utilize this waste and convert this waste into useful products. This will benefit society and will be helpful for keeping the environment clean. The objective is to optimize the bioreactor parameters and to keep the environment clean.

Sustainable power sources assume as essential to meet ambitious climate policy targets. Worldwide, around two million individuals need perfect and safe cooking fuel. They depend on traditional fuels like agricultural, farming waste and dried compost. In many countries, the biogas plants are very well able to provide livestock farmers with sustainable cooking fuel and potent organic fertilizer; this energy resource must be environmentally friendly. Anaerobic digestion is the most encouraging technology to accommodate this requirement due to the advantage of producing fuel gas and also producing smell-free remains-rich supplements, which can be utilized as fertilizers [6, 7]. Inside the scope of accessible sustainable power sources, bioenergy is likely to deliver the major share of future renewable generation. Already today bioenergy delivers about a third of all primary energy production from renewable sources. It is important to note that the primary product of interest for this study is the generated biogas and consequently energy production. Biogas can act as a fuel source to produce electricity and heat. It consists primarily of methane (50-60%), carbon dioxide (40-50%), and small traces of other gases such as hydrogen sulfide. The biogas can be fed directly into a modified engine-generator set that normally runs on fossil fuels such as natural gas and diesel fuel [8]. Biogas combustion results in the production of heat by the engine, which can be used to maintain the specific temperature range (mesophilic or thermophilic) of the anaerobic digester. Additionally, biogas combustion allows for the production of electricity used to provide electricity directly on-site or be sold to the local energy grid as a source of revenue [9, 10].

Biogas as a renewable energy source could be a substitute method of solving the issues of the energy crisis. Agriculture has a key significance in the Pakistan economy. Agriculture has remained the premise of Pakistan's economy as it offers employment to 45 percent of the populace and gives contribution to agro based industry. In Pakistan, relatively 20% of foreign exchange is spent on furnace oil import. Realization of the significance of biogas innovation will enhance the ordinary vitality sources in the rustic regions of Pakistan. An association did an examination on the possibility of a family unit biogas program in mid-2007. The result of the investigation revealed that Pakistan has one of the biggest unexploited biogas assets in the district and dependent on the accessibility of domesticated animals and reasonable climatic conditions, the specialized potential was assessed to be more than 5 million family unit biogas digesters in the nation. The aim of this study was to conduct a specialized survey of existing biogas plants developed crosswise over Pakistan over the previous years to encourage the arrangement of an execution plan for the proposed National Domestic Biogas Program. Data on the accompanying perspectives were gathered and examined by financial qualities of tested biogas families (populace design, family measure, occupations, arrive possessions, agrarian creation, domesticated animals proprietorship and instructive status), development, activity and upkeep of biogas plant. Effects of biogas on users and evaluation of best appropriate model(s) are to be dispersed under the structure of the proposed biogas program. Biomass is the most easily accessible and the least expensive energy resource. By the economic overview of Pakistan the biomass assets of Pakistan are shown in Table 1 [11, 12].

Table 1. Livestock population in Pakistan

Species	Livestock Population (Million)
Cattle	35.6
Buffalo	31.7
Sheep	28.1
Goat	61.5
Camel	1.0
Horses	0.4
Asses	7.0
Mules	0.2

Raw materials and products

In biogas plants, biogas can be delivered by utilizing various distinctive input substrates.

Natural materials are basical substrates for creating biogas and the key beginning stage for the generation procedure. There are seven groups of organic materials which are appropriate substrates. The domestic organic waste means separate gathered vegetable and fruit wastes, flowers, flower soil, eggshells, tea and coffee filters and other organic remains [13, 14]. The level of dry issue differs somewhere in the range of 10 - 30 %. The green and plant squanders hacking and scraps from cutting greenhouses or parks which do not contain wood make a difference (lignin). The public sewage slop extra from shared waste water treatment is ooze, which must be disinfected to be utilized for biogas generation. This sewage slop can contain phosphorus, nitrates and overwhelming metals. Experience demonstrates that slime from waste water treatment is appropriate in biogas plants, is, however, not considered as an amazing substrate. It is unlawful to utilize slop from non-open sources on account of the higher content of substantial metals or hereditarily adjusted living beings or hormones. The level of dry issue shifts somewhere in the range of 20 - 30 % [15].

The liquid or solid manure from animal cultivating is one of the basic substrates for the digestion process. Cow manure is best, while chicken fertilizer for instance has a high yield, yet may contain sand [16, 17]. Chicken compost can likewise be utilized for biogas creation. Chicken dung produces biogas quicker than some other substrates. The dry matter of a solid fertilizer changes somewhere in the range of 15 - 30% and of fluid excrement somewhere in the range of 5 - 7 % [18]. The energy crops are fundamentally developed on generally neglected fields, for example, corn, sudan grass, millet, white sweet-clover. The modern nourishment squander originates from sustenance and meat creation locales or procedures, for example, whey, potato squash, vegetable leftovers, brewer grains, apple marc. These sorts of substrates are typically entirely reasonable and do not contain unsafe substances. Substrates from meat generation, such as slaughterhouse squander, are useful natural materials yet require exceptional treatment to decrease wellbeing dangers and smell. The products are biogas, high-quality fertilizer and a potential source of energy like heat, light and electricity [15, 19].

Cow dung of generally dark magenta in colour is utilized as agricultural fertilizer. If not recycled into the soil by some species like earthworms and dung beetles, cow dung can dry out and stay on the field, making a territory of munching land which is unpalatable to domesticated animals. Nowadays dung may also be collected and used to produce biogas to generate heat and electricity. The gas is used in rural areas of Pakistan and elsewhere to provide a stable and renewable source of electricity [4].

The past several years have witnessed some energizing improvements that present a chance to give natural waste streams something to do in a lot bigger route towards giving a source of renewable energy to meet power, warmth and transportation energy needs. In light of the fact that when a fertilizer is joined with a higher-carbon source, for example, fats, oils or sustenance handling waste, ventures can significantly offer large biogas generation, and this can positively affect venture financial matters. There have additionally been undertakings that have spearheaded the capacity to evacuate carbon dioxide and other follow gases or contaminations to deliver an item that is identical to flammable gas and can be infused into the petroleum gas pipeline to meet warmth needs, or supply a source of fuel for the gaseous petrol vehicle use. These advancements distinctly exhibit the capacity of biogas energy frameworks to additional successful management of natural waste streams while providing a dependable and adaptable source of renewable energy source [16, 20].

Biogas production in Sweden

Sweden is on the top of the mountains in the production of biogas. It has almost 230 facilities for the production of biogas. Half of the production of biogas is from wastewater treatment plants. Since the ban on landfilling in 2005, the biogas production in landfills has reduced. However, new plants, mainly co-digestion plants, are being established. Sweden produces 1.4 TWh (terawatt hours) annually from its 230 facilities. Table 2 shows the type and number of plants in Sweden and the energy produced from biogas [21]. Sweden has the theoretical potential of producing biogas of more than 15 TWh/year, which is approximately 10 times than its production at this time. Many substrates are still considered residue or waste, so research is being done to use this substrate or waste to increase the production of biogas. Agriculture residue is showing great potential for the production of biogas. 7 TWh of biogas can be annually produced if Sweden uses 10% of their agriculture land. Table 3 shows the potential for biogas production [21].

The biogas production depends upon the substrate.If substrates have good nutrients and good potential, then production of biogas can be increased. Table 4 shows the production of biogas from different substrates, as tested in the laboratory, so these results are higher, and in the actual process, the production will be low [22, 23].

Biogas production can be greatly increased by using crops as a substrate. Table 5 shows the potential of some crops for producing biogas [8, 13].

Table 2. Number of different biogas plants in Sweden

Biogas Plant	Number	Energy in Biogas (GWh/year)
Waste water treatment plants	135	614
Co-digestion plant	18	344
Farm plants	14	16
Industrial wastewater	5	114
Landfills	57	298
Sum	**229**	**1387**

Table 3. Different substrates and their potential for producing energy

Substrate	Potential Biogas Production with Limitations* [TWh]	Total Biogas Potential [TWh]
Food wastes	0.76	1.35
Wastes from parks and gardens	0	0.40
Industrial waste and residue (including food industry)	1.06	1.96
Sludge from wastewater treatment plant	0.7	0.73
Agriculture residue and manure**	8.10	10.78
Total	**10.62**	**15.22**

*Taking into account limitations in today's technical and economic situation.
** 5.8 TWh of this potential origin from straw which requires pretreatment before digestion

Table 4. Production of biogas from different substrates and methane concentration

Substrate	TS [%]	Biogas Production		Methane Concentration [%]
		$[m^3.ton^{-1}$ TS]	$[m^3.ton^{-1}$ wet weight]	
Sludge from waste water treatment plants	5	300	15	65
Fish waste	42	1279	537	71
Straw	78	265	207	70
Sorted food waste	33	618	204	63
Liquid cattle manure	9	244	22	65
Potato helum	15	453	68	56
Slaughter house waste	16	575	92	63
Liquid pig slurry	8	325	26	65

Table 5. Different agricultural wastes and their methane production

Substrate	Harvest[1] [Ton/hand year]	TS [% of wet weight]	Methane Yield [Nm^3 methane/Ton wet weight]	Substrate Need [Ton/GWh]	Land Requirement [Ha/GWh]
Jerusalem artichoke[2]	60	22	48	1500	25
Maize	43	30	95	1070	25
Potato	26	25	100	1020	39
Sugar beet[3]	50	24	94	1090	22
Grass	22	35	95	1100	50
Wheat grain	5.2	86	370	300	58

[1]Harvest quantities are valid for the area of Malardalen.
[2]Data are valid for harvest of stem.
[3]Harvest quantities are valid for the area of Skane

Table 6. Difference between aerobic and anaerobic digestion

Aerobic Digestion	Anaerobic Digestion
It occurs in the presence of oxygen	It occurs in the absence of oxygen
It always releases CO_2 and H_2O	Its end product may vary, depending on the feed
High production of biological sludge	Less production of biological sludge
It yields at 36 ATPs	It yields at 2 ATPs

The potential of biogas in Pakistan

Pakistan's main source of income is through agriculture. An agricultural country must have a huge number of livestock and farms to fulfil its requirement and made a profit. Due to this huge amount of waste is produced in agricultural countries. Pakistan also produces a huge quantity of animal waste and agricultural residue. Pakistan produces daily almost 55000 tons of solid waste, 225000 tons of crop residue and almost 1 billion tons of animal manure. According to a survey done in 2016, Pakistan has livestock of around 56.9 million of cows, buffalos and bullocks. On average, 15 kg of dung are dropped daily by an animal. So the total amount of animal dung produced is around 854 million per day. If half of this quantity is used for biogas production almost 21.35 million m^3 of biogas can be produced, which also means that 450 million tons of bio-fertilizer are also produced per day. Also in 2016, 15 million layer-chicken and 528 million broiler chicken birds were breaded in Pakistan. Chicken dung can also be used for biogas production. Chicken dung produces biogas faster than some other substrates. One ton of layer-chicken and broiler chicken fresh dung can produce 170-200 m^3 of biogas. Dung containing bedding can produce about 100 m^3 of biogas from 1 ton. Pakistan has the potential of producing 8.8 to 17.2 billion m^3 of biogas per year (equivalent to 55 to106 TWh of energy) from livestock residue. Also, 5700 GWh of electricity can be annually produced from bagasse (the fibrous residue of sugarcane after its processing) [24, 25].

Aerobic digestion process

This is a process carried out in the presence of oxygen. The oxygen comes directly from the surrounding. Generally, by doing aerobic digestion, the end product is carbon dioxide and water. The carbon dioxide produces a greenhouse effect in the environment and for preventing this carbon dioxide is collected in a gas collecting system. If the feed contains nitrogen, phosphorus and sulfur, so the end products will be nitrates, phosphates and sulfates. The advantage of aerobic digestion process from start to end is that the it takes only 5 days. The end product of the aerobic digestion is safe for the environment and the personnel. The time and the effort required to convert any food to waste for aerobic digestion is on the top. The limitations of aerobic digestion process are due to the oxygen supplying cost and the generally poor dewatering characteristics of the sludge produced by aerobic digestion [26].

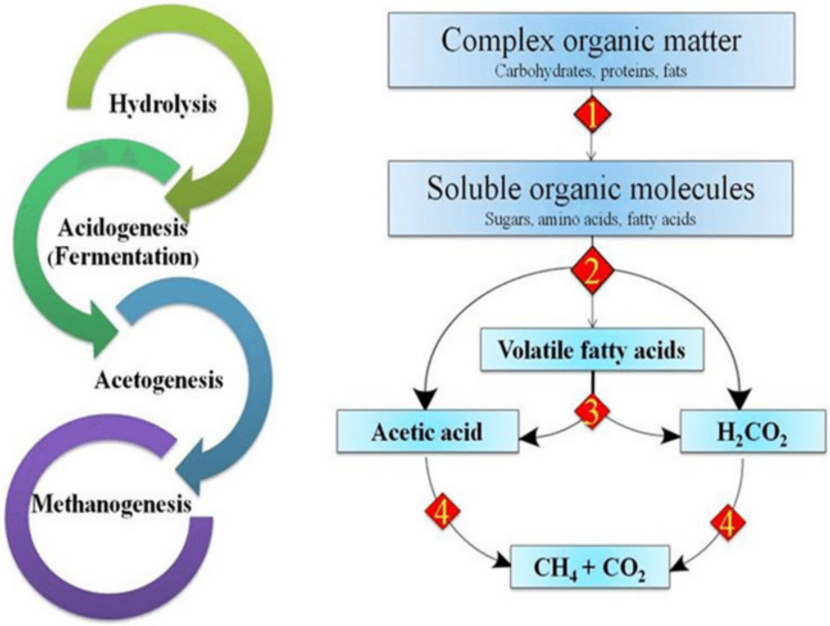


Fig. 2. Process of anaerobic digestion

Anaerobic digestion processes

This is a process carried out in the absence of oxygen. The basic purpose of the anaerobic digestion is to convert the waste to a useful product such as biogas that can be used as a fuel. The anaerobic digestion process is shown in Figure 2. The steps included in the formation of biogas through anaerobic digestion are: hydrolysis, acidogenesis, acitogenesis and methanogenesis [25, 27]. The steps are interlinked. The biogas formed by anaerobic digestion is high in percentage (50-75%). The end products of anaerobic digestion are carbon dioxide and methane. The quantity of gas produced depend on the amount of feed entered in the digester. The advantages of anaerobic digestion are that the wastewater pollutant is converted into methane, carbon dioxide and traces of biosolids, the biomass growth is much lower and low nutrients are required. The limitations of anaerobic digestion are that the exhaust gas coming from the gas engines requires treatment and cleaning of biogas to avoid corrosion [27]. The differences between aerobic and anaerobic digestion are shown in Table 6.

By considering the advantages and the limitations of both the processes, anaerobic digestion was selected, because there is no requirement of oxygen, fewer requirements of nutrients, a potential source of fuel, less production of biological sludge because the growth of the cell is slow. Anaerobic digestion is very cheap as compared to the aerobic digestion. It also has high treatment efficiency for the biodegradable sludge. The methane production in anaerobic digestion is in larger percentage as compared to the aerobic digestion. The residual sludge is also used as a soil conditioner [27, 28]. The series of biological processes in which the complex compounds can be broken down into the simplest compounds is shown in Figure 2. Anaerobic digestion works in the absence of oxygen. The end product is biogas that has very vast use: it is used to generate electricity, as a fuel, it is converted into renewable natural gas. Generally, the anaerobic digestion takes place in a sealed vessel that has an inlet valve for feed and a discharge valve; it also has a gas outlet point, it provides the agitator and the heater in the cold season (weather) to set the desired temperature in the vessel.

Hydrolysis is the first step in the production of biogas. In this process, complex polymers such as carbohydrates, fats and proteins are converted into simpler monomers such as amino acids, fatty acids and glycerol. This is a very important step determining the rate if the process of decomposing of the complex polymer is slow so the next three steps will be affected, that results in increasing the retention time. By hydrolysis carbohydrates are converted into sugars; fats are converted into fatty acids and proteins are converted into amino acids [28, 29].

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \quad (1)$$

After hydrolysis, the next step is acidogenesis; this is the continuation step in which the amino acids, sugars and fatty acids that are the product of hydrolysis are converted into acetates, hydrogen, carbon dioxide, traces of volatile fatty acids (VFA) and alcohols. The main products of acidogenesis are propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), acetic acid (CH_3COOH) and others.

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \quad (2)$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \quad (3)$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \quad (4)$$

After acidogenesis, the products of previous steps: hydrogen, carbon dioxide, formic acid, propionic acid and other simple acids are converted into acetic acid. This is an important acid as it directly produces methane. The acetogenesis process is done in the presence of acetogenesis bacteria used to produce acetic acid, hydrogen and carbon dioxide. It makes sure that the hydrogen produced in this step has partially low pressure which helps for the conversion of all acids. This type of low pressure is carried out by hydrogen scavenging bacteria [25].

$$C_6H_{12}O_6+2H_2O \rightarrow 2CH_3COOH+2CO_2+4H_2 \quad (5)$$

As the most important step in the production of methane in this stage the methanogenic bacteria convert the products of acetogenesis (acetic acid, hydrogen and carbon dioxide) into methane as shown in Figure 2. The following reactions take place:

$$CO_2+4H_2 \rightarrow CH_4+2H_2O \quad (6)$$

$$CH_3COOH \rightarrow CH_4+CO_2 \quad (7)$$

There are two conventional operational levels of temperature for the anaerobic digestions, to find species of methanogens in the digester. Mesophilic digestion is the type of anaerobic digestion taking place optimally around 30 - 38ºC, or at ambient temperature between 20ºC and 45ºC where the mesophiles are the primary microorganisms present. Thermophilic type of anaerobic digestion takes place optimally around 49 - 57ºC, or at elevated temperature to 70ºC, where thermophiles are the primary microorganisms present [25].

There are many parameters that have to be set in order to achieve maximum production of biogas. The parameters must be controlled in the desired range in order to obtain the complete and effectively breakdown by microorganisms. The temperature must be controlled in the desired range because the microorganisms need a suitable temperature environment to work; the methanogenesis phase is very sensitive to temperature as it affects the methanogens that produce methane. It also depends on the seasons. In the winter season, the digester is facing the sun, daytime is the time the measures are quickly be taken, because at the night time the temperature of the atmosphere is decreasing, so to prevent this the digester is covered with some clothes and the gas holder is covered with transparent polyethylene during the sunshine hours and insulating it in the off-shine hours, the temperature must be maintained at 30-40ºC. In anaerobic digestion, the temperature is divided into two types of conditions. In mesophilic conditions the operating temperature is between 30-38ºC, the mesophilic conditions require less input energy and are also less sensitive to shock load or toxic substances. The temperature which is favourable for this condition is 37ºC. The bacteria present in this condition are called mesophiles. The mesophiles are more efficient than thermophiles because most of the methanogens belong to mesophiles. The retention time for the mesophilic condition is 25 to 30 days. In thermophilic condition, the operating temperature is between 50-60ºC. The thermopiles are more efficient compared to the mesophiles because they take less retention time, but on the other hand, they require high energy input and are highly sensitive to a shock load. The yield of thermophilic condition is high compared to mesophilic one, the retention time for the mesophilic condition is 15-20 days [11, 25, 27].

Agitation plays an important role in the anaerobic process. By agitation, the feed and microbes that are present in digester mix well and also the temperature is uniformly distributed throughout the feed in the vessel. Mixing increases the contact area and provides a uniform concentration of products and prevents scum formation. The pH has a very high impact on the stability of anaerobic digestion. The pH is a measure of acidity and alkalinity of a solution; if pH is 7.0 the solution is neutral, if pH is less than 7.0 it is acidic. The pH range where a digester performs well is from 6.8 to 7.4. If the pH is less than 6.8 so the production rate is decreased and if pH is greater than 7.4 the same results. To stabilize the alkalinity we use potassium bicarbonate or calcium carbonate (lime). The formation of carbon dioxide and fatty acids affects the pH of the digester. Most of the research papers show that the effective pH for digestion is in-between 6.8-7.2. It was found that above pH 5.0 the efficiency of production of methane is increased by 75% [30].

The effect of total solid content in the anaerobic digester is low: solid systems have less than 10% total solids, medium solid systems have less than

15-20% total solid and high solid systems have 22-40% total solid content. The carbon-to-nitrogen ratio plays an important role in the production of biogas. For optimal growth of bacteria, it should be noticed that the nutrients are provided with desirable concentration. Nitrogen is the building structure of the cell; the low C/N ratio means formation of ammonia and inhibits the formation of methane. C/N ratio depends on the feed composition. The optimal C/N ratio was found to be 15:1 in case of a cattle dung and 25:1 to 30:1 in general, as shown in Table 7. A very high C/N ratio means shortage of nitrogen [31].

Light has a very important effect on the production of methane. It inhibits the production of methane, that is why all digestion reactors are placed in darkness and sprayed in black color to prevent the light.

METHODOLOGY

The concept of bioreaction or "fermentation" was initially not known to humanity, but humans were taking the advantages of its results. Bread, cheese, wine and beer were all made by a process traditionally known as fermentation (a little-understood process successful more by chance than design) — the failure and frustration of the French vintners who found that they often produce vinegar, not wine. This led the famous French chemist and microbiologist Louis Pasteur to study the fermentation at their request. Pasteur discovered that the biological activity of a microscopic plant called yeast causes the fermentation and its results. When unwanted microbes infiltrated the wine and fed on alcohol produced by the yeast, the microbes left behind distasteful and harmful wastes. Thus, flavour of the wine is ruined. Pasteur's work revolutionized the bioreaction industry because once the process is identified and understood, it can be controlled [30]. The scope of bioengineering has grown to the industrialization of wine, cheese, beer and milk to biotechnology's newer products like antibiotics, enzymes, steroidal hormones, vitamins, sugars and organic acids. A system in which biological conversion is affected is called a bioreactor. The bioreactors referred here include only mechanical vessels in which organisms are cultivated in a controlled manner and products are formed through specific reactions. Bioreactors are different from chemical reactors because they are specially designed to influence metabolic pathways. Chemical reactors whose design and models can be used as bioreactors include continuous stirred-tank reactor, continuous flow stirred-tank reactor, plug flow reactor and fluidized bed-reactor [30]. More severe consequences are posed by deactivation of biomass than chemical upset. An incubation period is required by all bioreactions for the establishment of the environment which favours the bioreactor for production of microbes. The bio-reaction can take 10-20 days for completion. Most of the bioreactions are done in batch reactors. The first phase is usually sterilization; after that enzyme culture is developed for the production of microbes. During the reaction time enzyme, substrate and product concentration can vary. This can be avoided by proper mixing and proper temperature maintaining. For aerobic reaction, a continuous supply of oxygen is provided.

Table 7. Carbon-to-nitrogen ratios of organic materials

Average carbon-to-nitrogen (C:N) ratios for organic materials			
Greens/ Nitrogen	C:N Ratio	Browns/ Carbon	C:N Ratio
Pig manure	5-7:1	Leaves	30-80:1
Poultry manure (fresh)	10:1	Cornstalks	60:1
Alfalfa or sweet clover hay	12:1	Straw	40-100:1
Vegetable scraps	12-20:1	Bark	100-130:1
Poultry manure with litter	13-18:1	Paper	150-200:1
Coffee grounds	20:1	Sawdust	400:1
Grass clippings	12-25:1	Wood chips	800:1
Cow manure	20:1		
Horse manure	25:1		
Horse manure with litter	30-60:1		

The advantages of the batch reactor are: contamination of reactor is minimized due to the long growth period, low capital investment, higher flexibility with products and high conversion. The disadvantage of the batch reactor is the time-consumption due to filling, heating, sterilization, emptying and cleaning, the greater expanse for establishing a new environment for new products and industrial hygiene risk. In the continuous reactor, the environment for the production of microbes is continuously fed to the bioreactor to maintain the steady state and product is continuously drawn. The advantages of the continuous reactor are: potential for automating the process, low labour cost, lower time consumption and constant product quality. The disadvantages of the continuous reactor are: lower flexibility, uniform supply of reactors and substrates required, high capital cost [33].

Designing of a bioreactor

The most important task is to control and have a positive influence on the bioreaction in the effective bioreactor. The key points which are to be focused during the designing of a bioreactor are: controlled temperature, maintained pH, appropriate amount of substrate, availability of water, salts, vitamins, oxygen (for the aerobic process), gas outlet and collection, products and side products collection and separation [33]. The reactor was made up of stainless steel because bioreaction required acid or base for control of pH and also produced acidic gases, due to which metal oxides were formed in the bioreactor, and it became corroded. Also, it had many leakages, due to which biogas cannot be contained in the reactor nor collected.

Considering the design of a pervious batch a simple first pilot plant was fabricated. The bioreactor was made of plastic so that contamination may not happen. In this reactor, only inlet and outlet for biomass is provided and also a gas outlet for its collection. No agitation was provided, temperature was not controlled, and no constant pH was maintained. As a result, the desired results were not obtained. Due to the absence of key factors in designing the bioreactor, the first pilot plant was not successful. Therefore, a second pilot plant was fabricated and was provided with key factors like temperature control, pH control and proper agitation.

Reactor designing on software NX 8.0 and specification

NX Unigraphics (U-G) is an advanced high-end CAD/CAM/CAE software package initially developed by Unigraphics, but since 2007 by Siemens PLM Software. It is used for designing (parametric and direct solid modelling), engineering analysis (dynamic, static, electro-magnetic, thermal, using the finite element technique, and fluid using the finite volume technique) and manufacturing a finished design by using involved machining modules. The 3D-diagrams are shown in Figure 3. Figures 4 to 6 show the top, side and front views of the bioreactor, agitator and cup. The reactor specification is given in Table 8.

Table 8. Equipment with specifications

Equipment	Specification
Reactor vessel	19.0 liters
Electric heater	500 watts
Slurry inlet pipe	2.0 inches
Slurry outlet pipe	1.25 inches
Gas outlet pipe	0.5 inches
Acid or base inlet pipe	0.5 inches
Slurry inlet valve	2.0 inches ball valve
Slurry outlet valve	1.25 inches ball valve
Gas outlet valve	0.5 inches ball valve
Length of agitator fan	23.3 inches
Plastic tub (for water bath)	33 liters
Thermocouple	T-type

Calculations for heating coil for bioreactor by the last batch

For the calculation of the heating coil Eq. (8) was used:

$$h_b \frac{dv}{k} \times \left(\frac{\mu s}{\mu}\right)^{0.14} = 0.55 \left(\frac{L^2 N}{\rho \mu}\right)^{0.67} \times \left(\frac{Cp}{\mu k}\right)^{0.25} \quad (8)$$

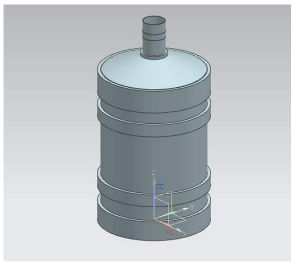
Since the agitator used in that bioreactor was of paddle type, the constant will be 0.36 and the index will be 0.67, if Reynold number condition is satisfied [1, 33].

$Stainless\ steel\ 304 = K = 14\ W.m^{-1}K^{-1}$

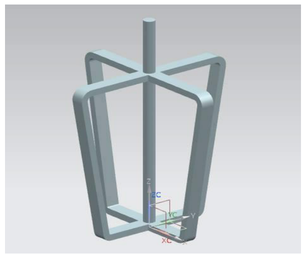
$\mu_{50°C} = 0.000547\ Pa.s$

$Cp_{50^oC} = 4.182\ KJ.kg^{-1}K^{-1}$

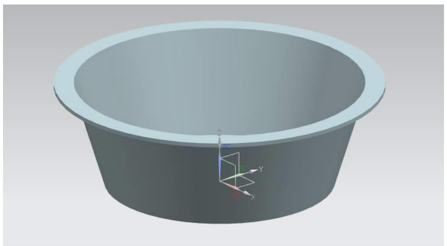
$\rho_{50°C} = 988\ kg.m^{-3}$



(a)



(b)



c)

Fig. 3. 3D-diagram: (a) Bioreactor (b) Agitator (c) Moving cups

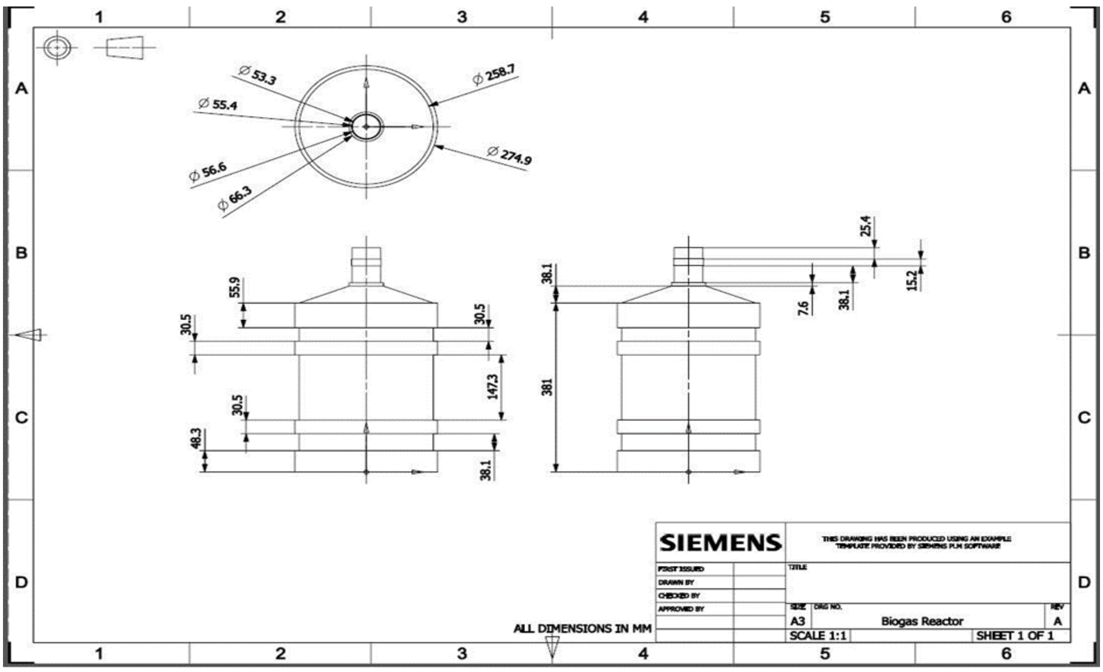


Fig. 4. The top, side and front view of the bioreactor

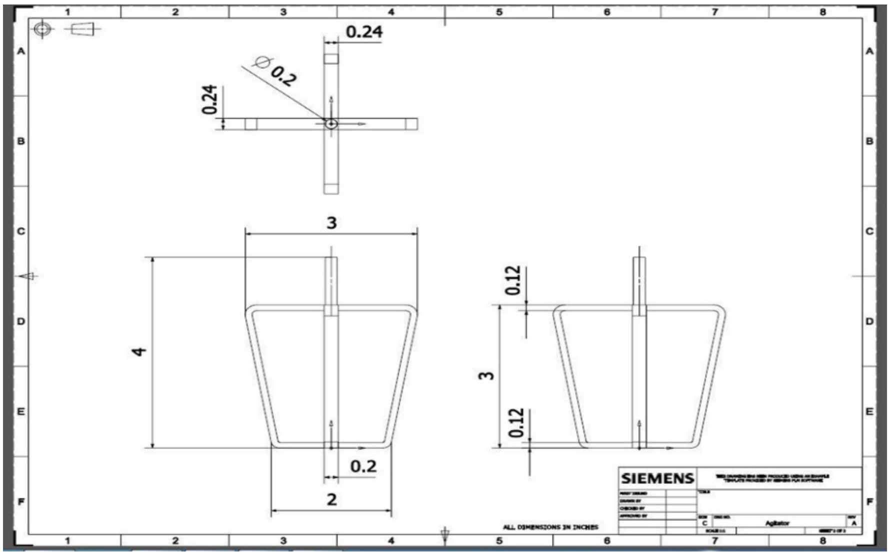


Fig. 5. The top, side and front view of the agitator

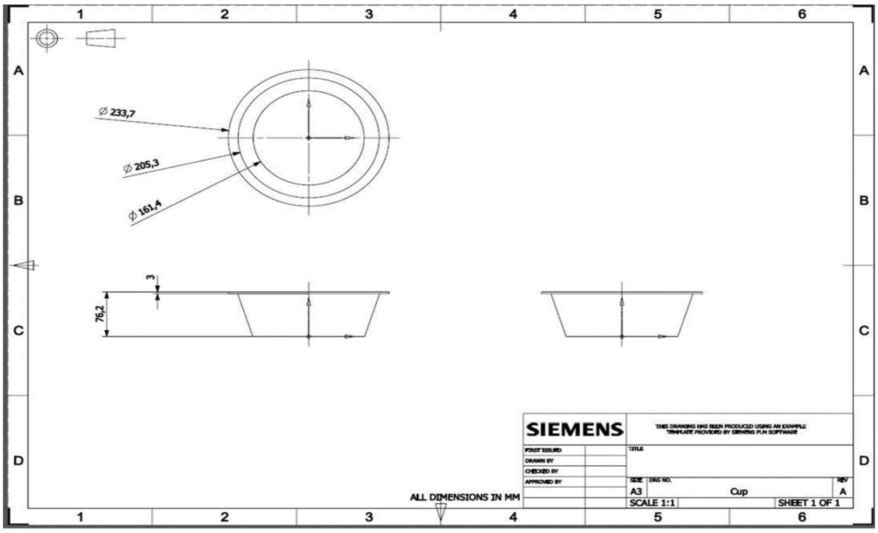


Fig. 6. The top, side and front view of cups

$D_t = Diameter\ of\ coil = 0.0187\ m$

$Q = Volumetric\ flowrate\ of\ water\ in\ coil = 2L.min^{-1} = 3.333 \times 10^{-5} m^3.sec^{-1}\quad (assumed)$

$$V = \frac{Volumetric\ Flowrate}{Area\ of\ Coil} = \frac{3.333 \times 10^{-5}}{\frac{3.124\ (0.0187)^2}{4}}\ 0.12134\ m.s^{-1} \quad (9)$$

$$Re = \frac{\rho V Dt}{\mu} = \left(\frac{988 \times 0.12134 \times 0.0187}{0.000547}\right) \quad (10)$$

$Re = 4098.40823$

Since Reynold number is greater than 4000 the above equation can be used.

L = Length of agitator = 0.304 m, N = Revolutions per second = 0.1 rps (assumed), dv = Diameter of reactor = 0.776 m and h_b = Heat transfer coefficient of coil.

$$h_b \frac{dv}{k} \times \left(\frac{\mu s}{\mu}\right)^{0.14} 0.36 \left(\frac{L^2 N \rho}{\mu}\right)^{0.67} \times \left(\frac{Cp\mu}{k}\right)^{0.25} \left(\frac{0.0929 * 0.1 * 9.88}{0.000547}\right)^{0.67} \times \left(\frac{4.182 * 0.000547 * 1000}{14}\right)^{0.25}$$

$$h_b = 6.494 \times (677.0213) \times (0.6358) \quad (11)$$

$h_b = 2795.793127\ W.m^{-2}K^{-1}$

Calculations for agitation

The diameter of the impellor is 14 cm that is run by wind as shown in Figure 7. The calculation shows the force required by agitator to rotate [1].

The distance cover by the bowl to rotate the agitator is given by:

$$S = R\theta \quad (12)$$

$R = 60\ cm\ or\ 0.6\ m$

$\theta = 120^o or\ \frac{2\pi}{3}$

So,

$S = 0.6 \times \frac{2\pi}{3} = 1.256m$

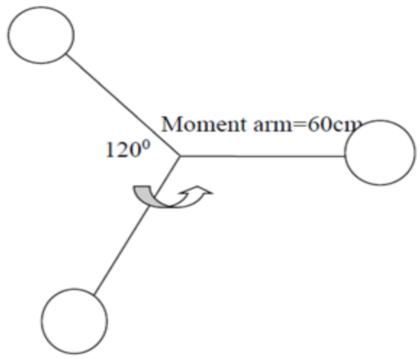


Fig. 7. Wind turbine for agitation

Density of slurry = 1047 kg.m^{-3} at 50^{o}C, Density of air = 1.225 kg.m^{-3} at 50^{o}C, Tank diameter = 0.226 m, Diameter of agitator = 0.14 m and Diameter of bowl = 16 cm. In this study, use two bowl of diameter 16 cm so the volume to trap the air is:

$$V' = 3 \times \frac{4\pi r^3}{3} \quad (13)$$

$V' = 3 \times \frac{4\pi(0.08)^3}{3}$

$V' = 6.434816 \times 10^{-3} m^3$

The volume of half of the sphere is:

$$V_b = \frac{V'}{2} \quad (14)$$

$V_b = \frac{6.434816 \times 10^{-3}}{2}$

$V_b = 3.217408 \times 10^{-3}$

$$Mass\ of\ air = Density\ of\ air \times\ Volume\ of\ bowls \quad (15)$$

$M_a = 1.22 \times 3.217408 \times 10^{-3}$

$M_a = 3.92523776 \times 10^{-3} kg$

$$Mass\ of\ slurry = Density\ of\ slurry \times Volume\ displace\ by\ agitator\ in\ tank \quad (16)$$

$$Volume\ displace\ by\ agitator = v = \pi r^2 \times width\ of\ agitator \quad (17)$$

$M_f = 1047\pi(\frac{0.0762}{2})^2 \times 0.02$

$M_f = 0.0955\ kg$

Velocity after the collision of air with bowls, according to the law of conservation of momentum [1, 33]:

$$V_f = M_a \left(\frac{Avg\ velocity\ of\ wind}{M_a + M_f}\right) \quad (18)$$

$V_f = 8(\frac{3.92523776 \times 10^{-3}}{3.92523776 \times 10^{-3} + 0.0955})$

$V_f = 0.0394 m.s^{-1}$

Acceleration due to change in velocity:

$$A = \frac{Vf^2 - Vi^2}{2S} \quad (19)$$

$A = \frac{0.03947^2 - 8^2}{2 \times 1.256}$

$A = -25.47 m.s^{-2}$

Acceleration is decreasing that why it is negative.

Force on bowls to rotate

$$F = M_f\ A \quad (20)$$

$F = 0.0955 \times 25.47$

$F = 2.432385\ N$

Number of rotations per minute:

$$V = \pi\ D\ N \quad (21)$$

$0.0394 \times 60 = \pi \times 0.0762 \times N$

$N = 10\ rpm$

The force and number of rotations shown above can be changed by changing bowl diameter and agitator diameter.

RESULTS AND DISCUSSION

In this research, fish waste was used along with sewage water in a ratio of 1:1. The experiment was performed in 1.5 litre- bottles placed in a dark area.

The fish waste has great ability to produce biogas as compared to others. Co-digestion of manure with fish can give an optimum C/N ratio that helps in biogas production [19, 31]. The important characteristics of fish wastes, found in the study are given in Table 9.

Table 9. Characteristics of different fish wastes

Names	C.O.D. (ml.l^{-1})	B.O.D. (ml.l^{-1})	T.S. (ml.l^{-1})
Shrimp	3300	2000	900
Crab	6300	4460	620
Oysters	500-2000	250-800	200-2000
Tuna	1600	200	500
Salmon	300-550	250-2600	120-1400
Catfish	700	340	400

When using the liver of pink salmon, the moisture contents, lipids fats and proteins are 77%, 3.3% and 16%, respectively. When using the head of trout fish the moisture lipids, fats and proteins fractions are 70%, 12% and 14% respectively. When using intestines of trout fish, we have 56%, 35% and 8% respectively. Some factors are most important to control, such as pH, temperature, mixing, and ammonia inhibition [19]. There are lots of problems related to the first experiment. The most important problem was the fluctuation of temperature that was not controlled throughout the experiment. The temperature range to be maintained was 28-34ºC. There was no pH controlling device neither. In this experiment no agitation was provided. The results obtained were that gas was produced, however, it had not enough methane content to burn.

Then, a new experiment was started which is known as co-digestion. Co-digestion of cow dung and banana skin with water was done. The ratio of cow dung, banana skin and waster was 60:25:15. The main purpose of co-digestion was to maintain the C/N ratio at the optimum point. Co-digestion is important when we have a waste of low C/N ratio so another waste was added to enhance the C/N ratio. The increase in C/N ratio reduces the effect of ammonia and maximizes the methane potential [19, 34]. The time period of this experiment was 25 days. The feed for the co-digestion experiment was: mass of banana skin 2.5 kg, mass of cow dung 6 kg and 1.5 l of sewage water. The temperature was ambient (fluctuation was observed), pH of water was 7.6, and overall pH was 8 (needed to be adjusted). This experiment was also started with the experiment above. Similarly, continuous agitation was not provided and temperature and pH were not controlled. Similar results were obtained on gas production with no enough methane content to burn.

Cow dung and sewage water

In this experiment cow dung and sewage water were used. Water was 2.22607 l, and cow dung was 4.34921 kg. Water content plays a vital role in bacteria activities and growth. Bacteria movement and activity are determined by the water content in the digester. As the feed entered the reactor oxygen was removed by purging with nitrogen gas that is inert and anaerobic digestion was carried out. No particular temperature was maintained during this experiment. It was performed at variable temperatures. The hydraulic retention time of this experiment was 25 days. The average characteristics of cow dung are shown in Table 10.

The first stage was the pretreatment of organic waste to remove the impurities with a view to enhance bacterial growth. The second stage was the mixing of solids with water and homogenizaion of the slurry. The third stage was the batch digestion in the absence of oxygen. The fourth stage was the purging of nitrogen to displace remaining oxygen in the sealed reactor.

Table 10. Average properties of cow dung

Parameters	Composition
TS (mg.l^{-1})	156
VS (mg.l^{-1})	32.5
COD (mg.l^{-1})	2200
NH_3-N (mg.l^{-1})	680
pH	7.1-7.4
Moisture (%)	41.4

This experiment was conducted for 25 days. Although continuous agitation was not provided, high ambient temperature was maintained because at that time the temperature in Karachi was around 45-50ºC. The results obtained showed a high methane content to produce the flame, as shown in Figure 8. So this proves that for production of biogas temperature plays an important role.

The pH decreased during the hydrolysis process in the reactor. The sudden decrease in pH created toxicity for the methanogenic bacteria that caused failure of the experiment. As the organic matter is reduced to volatile fatty acids and accumulated during digestion, so pH tends to decrease. If pH is below 6.5 the methane production decreases. As volatile fatty acids consume methane and thus acids are destroyed, pH of the digester increases.

Fig. 8. Flame test of cow dung and sewage water

There is a variation in temperature and control is not easy. It was observed that in the mesophilic temperature experiment a small tolerance (-3 to +3) may create 30% decrease in biogas production. Especially in thermophilic temperature conditions the system is very sensitive, and tolerance of about (-1 to +1) was observed. At 45 to 47°C the rate of reaction is low due to mesophilic and thermophilic microorganisms collision [10, 27]. Limits of temperature and pH for mesophilic digestion are shown in Table 11.

Table 11. Limits of temperature and pH for mesophilic digestion

Parameter	Hydrolysis/ Acidogenesis	Methanogenesis
Temperature	25-35°C	Mesophilic 30-40°C
pH value	5.2-6.3	6.7-7.5

Another problem is the agitation of the slurry at proper rpm. Because a slurry in a reactor needs to be continuously agitated to homogenize the bacteria with the substrate and prevent from partials settlement. Ammonium inhibition must be considered. Ammonium is toxic to mesophilic methanogenic bacteria at a concentration over 300 mg/l. The thermophilic process is more sensitive to ammonium. For the thermophilic process, ammonium shows the inhibitory concentration to be over 4900 mg/l when using fat substrate. From organic nitrogen, the ammonium is created during proteins degradation. Quality of cow dung was not constant place to place. Some of it contains poisonous contaminants; metals, inorganic substances, and non-degradable waste [10, 27]. No such nutrients were detected that was meaningful for biogas production. The material of the reactor created a hazard for bacteria, and microorganism performance decreased. The decrease in the activity of organisms decreased the gas production. The extra time that is above the experiment duration time may degrade the methane gas and increase the carbon dioxide gas.

Waste solids such as food, silage, sewage waste that contain unique properties like volatile solids, optimum C/N ratios, pH range (6 to 7) better BOD, are good for biogas production. Protein-rich substrate is good because the optimally pH is maintained in the process stages. The substrate that contains fats increases the hydrolysis rate, but acetogenesis in limited thermophilic conditions is required. To control the pH, a separate device was introduced. If the pH increases or decreases, dilute hydrochloric acid for lower pH and sodium hydroxide for higher pH, respectively, was added. A pilot reactor of 19 l water cane was introduced that prevents methane gas from poisoning and minimizes the external impurities. To homogenize the feed slurry in the reactor to enhance the microorganisms activities, the reactor was equipped with anchor type agitator. This agitator does not run by an electric motor, but by the wind. Gearbox may be used to give power to the agitator. To control the temperature in the reactor, the latter was equipped with an electric heater with a bathtub that maintains the temperature in the range of 45 to 55°C, thermophilic conditions. Thermophilic digestion is about 10-15 days. Artificial nutrients and chemicals were introduced to enhance the activities of microorganisms. Yoghurt water and animal blood can increase the growth of bacteria because these materials have high BODs to degrade into methane producing substances. Regeneration time for microorganisms in the bioreactor is shown in Table 12. For gas collection, the motorbike tubes should be replaced with cylinders or glass bottles for gas because the polymer tubes may create impurities and react to forming non-favourable gases.

Table 12. Duration of different processes in the bioreactor

Process	Duration
Acidogenesis	Less than 36 h
Acitogenesis	80 - 90 h
Methanogenesis	5-16 days

In this experiment cow dung and sewage water were used with continuous agitation. Also, the temperature was being controlled, and constant pH was being maintained. 5.5448 kg of cow dung and 4 l of water were used. This experiment was done in the 2nd reactor with continuous agitation. The results obtained were quite remarkable: biogas was produced in 15 days. In cow dung and sewage water it took 25 days to produce biogas. So, by continuous agitation, the production time of methane production can be reduced. So this is also an optimizing parameter.

Another experiment was done with cow dung and water using 6.9899 kg of cow dung and 4.2708 l of water. In this experiment water displacement technique was used to find out the flow rate. This experiment was also conducted at the same conditions as the above experiment, however, this time the production rate of biogas was measured. For this, the water displacement method or the volume displacement method was used. The gas produced contained methane, carbon dioxide and hydrogen sulfide. The data for the production of biogas for 5 days are shown in Figure 9.

The result obtained from cow dung and sewage water in bioreactors with and without agitation showed that biogas was produced in both cases but the time required to produce is different.

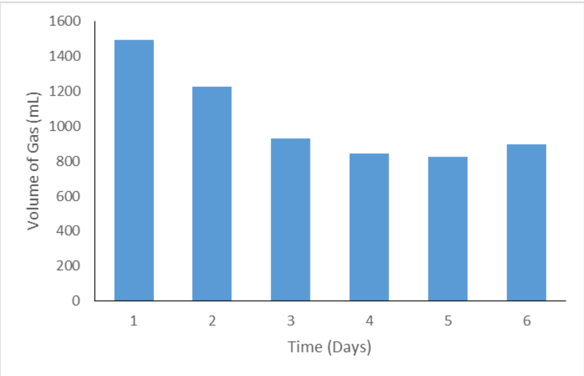


Fig. 9. Production of biogas with time

CONCLUSION

Pakistan has the potential of producing 8.8 to 17.2 billion m^3 (55 to 106 TWh of energy) of biogas per year from just livestock residue. In this study cow dung and sewage water was used with continuous agitation for the production of biogas. The results obtained were quite remarkable and the product had high methane content to produce a flame. The results obtained showed that from cow dung and sewage water in bioreactors with and without agitation, biogas was produced in both cases but the production time was different. In the mesophilic temperature experiment a 30% decrease in biogas production was observed, especially in thermophilic temperature conditions, the system is very sensitive and tolerable. The biogas was measured by the water displacement method or the volume displacement method. The gas produced contains methane, carbon dioxide and hydrogen sulfide. The future recommendation is to fabricate a proper digester with an agitator, heating mechanism and pH controlling device. Amine solvent should be used for absorption of carbon dioxide formed during the process.

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REFERENCES

1. Y. A. Hilal, F. S. Atalay, *Energ. Source. Part A.*, **25**, 1063 (2010).
2. D. Divya, L. R. Gopinath, P. Merlin Christy, *Renew. Sustain. Energ. Rev.*, **42**, 690 (2015).
3. V. Kirubakaran, V. Sivaramakrishnan, S. Shanmugapriya, M. Premalatha, P. Subramanian, *Energ. Source. Part A*, **31**, 1700 (2009).
4. P. A. Ukpai, M. N. Nnabuchi, *Adv. Appl. Sci. Res.*, **3**, 1864 (2012).
5. O. Yaldiz, S. Sozer, N. Caglayan, C. Ertekin, D. Kaya, *Energ. Source. Part A.*, **33**, 1802 (2011).
6. K. Mokobia, E. U. Ikhuoria, D. Olugbemide, *Int. J. Basic Appl. Sci.*, **1**, 258 (2012).
7. Y. Singhal, S. K. Bansal, R. Singh, *Int. J. Emerg. Sci.*,, **2**, 405 (2012).
8. C. Zhang, H. Su, J. Baeyens, T. Tan, *Renew. Sustain. Energ. Rev.*, **38**, 383 (2014).
9. A. Effuggi, D. Gelosa, M. Derudi, R. Rota, *Combust. Sci. Tech.*, **103**, 481 (2008).
10. P. Vindis, B. Mursec, M. Janzekovic, F. Cus, *J. Achiev. Mater. Manuf. Eng.*, **36**, 192 (2009).
11. F. Oliveira, K. Doelle, *J. Food Process. Technol.*, **6**, 1 (2015).
12. Y. Lee, S.-W. Oa, *J. Mater. Cycles Waste Manag.*, **18**, 201 (2015).
13. Z. Yong, Y. Dong, X. Zhang, T. Tan, *Renew, Energ.*, **78**, 527 (2015).
14. S. Pavi, L. E. Kramer, L. P. Gomes, L. A. S. Miranda, *Bioresour. Technol.*, **228**, 362 (2017).
15. I. R. Ilaboya, F. F. Asekhame, M. O. Ezugwu, A. A. Erameh, F. E. Omofuma, *World Appl. Sci. J.*, **9**, 537 (2010).
16. P. Abdeshahian, J. S. Lim, W.S. Ho, H. Hashim, C.T. Lee, *Renew. Sustain. Energ. Rev.*, **60**, 714 (2016).
17. H. Afazeli, A. Jafari, S. Rafiee, M. Nosrati, *Renew. Sustain. Energ. Rev.*, **34**, 380 (2014).
18. A. N. Matheri, S. N. Ndiweni, M. Belaid, E. Muzenda, R. Hubert, *Renew. Sustain. Energ. Rev.*, **80**, 756 (2017).
19. X. Wang, G. Yang, Y. Feng, G. Ren, X. Han, *Bioresour. Technol.*, **120**, 78 (2012).
20. P. Merlin Christy, L. R. Gopinath, D. Divya, *Renew. Sustain. Energ. Rev.*, **34**, 167 (2014).
21. B. Zhu, P. Gikas, R. Zhang, J. Lord, B. Jenkins, X. Li, *Bioresour. Technol.*, **100**, 1122 (2009).
22. K. Hagos, J. Zong, D. Li, C. Liu, X. Lu, *Renew. Sustain. Energ. Rev.*, **76**, 1485 (2017).

23. R. Campuzano, S. Gonzalez-Martinez, *Waste Manag.*, **54**, 3 (2016).
24. X. Wang, G. Yang, F. Li, Y. Feng, G. Ren, *Waste Manag. Res.*, **31**, 60 (2013).
25. H. W. Yen, D. E. Brune, *Bioresour. Technol.*, **98**, 130 (2007).
26. P. Intanoo, P. Rangsanvigit, P. Malakul, S. Chavadej, *Bioresour. Technol.*, **173**, 256 (2014).
27. B.S.U.I. Abubakar, N. Ismail, *ARPN J. Eng. Appl. Sci.*, **7**, 169 (2012).
28. I. M. Nasir, T. I. M. Ghazi, R. Omar, A. Idris, *Energ. Source Part A.*, **36**, 1476 (2014).
29. I. Muhammad Nasir, T. I. Mohd Ghazi, R. Omar, *Appl. Microbiol. Biotechnol.*, **95**, 321 (2012).
30. C. M. Ajila, S. K. Brar, M. Verma, R. D. Tyagi, S. Godbout, J. R. Valero, *Crit. Rev. Biotechnol.*, **32**, 382 (2012).
31. L. Alejo-Alvarez, V. Guzman-Fierro, K. Fernandez, M. Roeckel, *Environ. Technol.*, **37**, 2865 (2016).
32. B. Wu, *Comput. Electron. Agr.*, **93**, 195 (2013).
33. O. A. Aworanti, S. E. Agarry, O. A. Arinkoola, V. Adeniyi, *Int. J. Eng. Sci. Tech.*, **3**, 573 (2011).
34. A. Shilton, N. Powell, A. Broughton, C. Pratt, S. Pratt, C. Pepper, *Environ. Technol.*, **34**, 2491 (2013).