PRODUCTION OF BIOGAS BY BIOMETHANATION OF OILCAKE

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ABSTRACT - *Energy becomes a major political and economical role to play in the modern society. Energy consumption is increasing at a phenomenal rate. Current supply of energy depends on non-renewable fuels such as oil, gas and coal formed naturally beneath the earth crust. However, fossil fuels are getting depleted now. In today's energy demanding life style, there is a need for exploring and exploiting new sources of energy which are renewable as well as eco-friendly which is a must. 140000 MT/Day of Municipal Solid Waste (MSW) is being generated, requiring 1750 acres of land filling. Rapid industrialization and population explosion has led to generate thousands of tons of MSW daily. Various potential merits of Biomethanation like reduction in land requirement for disposal and preserves environmental quality. Biomethanation can serve as a potential waste-to-energy generation alternative energy [3]. Biomethanation of Municipal Solid Waste will drastically reduce the emission of methane and carbon*.

Key words: Municipal Solid Waste, Biomethanation, Energy, Environmental quality, Methane

1. INTRODUCTION

Biogas technology provides an alternate source of energy and is hailed as an appropriate technology that meets the basic needs. Using organic wastes, energy and manure are derived. Biogas is produced from organic wastes by concerted action of the anaerobic bacteria. The anaerobic process is used to treat organic wastes like sewage sludge, organic farm waste, commercial and industrial wastes. The outcome biogas is upgraded by removing carbon dioxide and water vapour and then used to produce heat and electricity. The digestate is used as manure in agriculture. This technology offers a very attractive route to utilize certain categories of biomass for meeting partial energy needs. In fact proper functioning of biogas system can provide multiple benefits to the users and the community resulting in resource conservation and environmental protection [1]. As a result of anaerobic degradation of sludge, biogas is produced. This is one of the oldest techniques used by industries to stabilize the sludge activity [7]. This process is carried out under microorganisms of size (200-500nm) and this depends on various chemical factors like pH, temperature, C/N ratio, etc. Thus there is a need to improve the overall efficiency of anaerobic digestion process in the biogas plants [1]. High efficiency of gas can be achieved by changing the operational parameters and adjusting the nutrients to microorganisms.

1.1. Anaerobic digestion (AD) process

This process is also called as biomethanation, in which large number of organic waste are isolated and fed into a closed container (digester) under anaerobic conditions, the wastes undergoes bio-degradation (with the help of anaerobic bacteria) and produces methane- rich biogas and effluent. The biogas production ranges from 75- 180 m^3/ tons of wastes. The biogas can be utilized as fuel, cooking/ heating applications, turbine for generating power and electricity. The remaining digestate and effluents can be used manure and soil conditioner based on its nutrient composition [4].

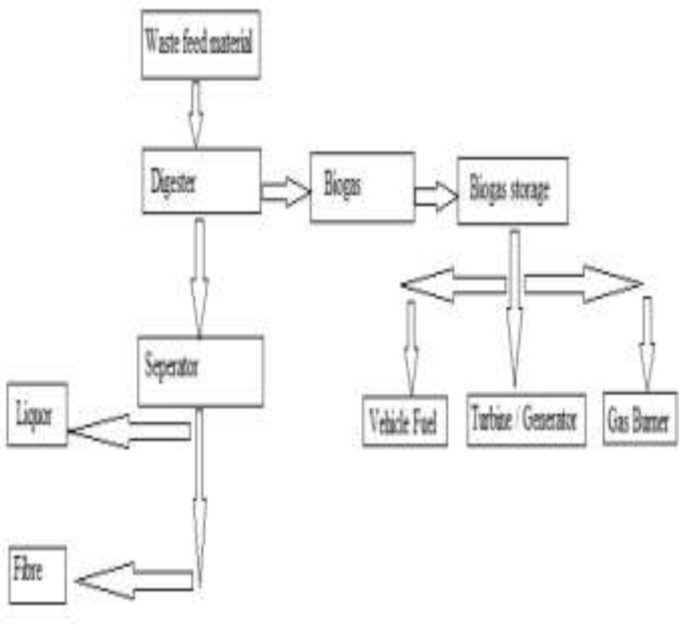

Fig1: Process Flow chart

1.2. Mechanism process

There are three main stage processes involves in anaerobic digestion process first stage is hydrolysis where complex materials are hydrolyzed and fermented into simple fatty acids, alcohol, carbon dioxide, ammonia and sulphides. This step usually involves enzyme-mediated transformation of insoluble organic material like proteins, lipids, nucleic acid, fats, polysaccharides, etc into soluble organic materials by anaerobes such as clostridia and streptococci. Second stage is acetogenesis process where acetogenic bacteria converts organic acids like propionic acid and butyric acid into acetic acid[2][3]. Third stage is methanogenesis process, where acetic acid, and carbon-dioxide are converted into methane, hydrogen and carbon-dioxide by methanogenic bacteria (methanosacrina, methanothrix, methanococcus).

1.3. Biomethanation

Process and mechanism of biomethanation

Fundamentally, the anaerobic digestion process can be divided into three stages with three distinct physiological groups of micro-organisms:

Stage I: hydrolysis

It involves the fermentative bacteria, which include anaerobic and facultative micro-organisms. Complex organic materials are hydrolyzed and fermented into fatty acids, alcohol, carbon dioxide, hydrogen, ammonia and sulphides. The first step usually involves the enzyme-mediated transformation of insoluble organic material and higher molecular mass compounds such as lipids, polysaccharides, proteins, fats, nucleic acids, etc. into soluble organic materials, i.e. to compounds suitable for the use as source of energy and cell carbon such as monosaccharide, amino acids and other simple organic compounds. This step is called the hydrolysis and is carried out by strict anaerobes such as Bactericides, Clostridia and facultative bacteria such as Streptococci, etc.

Stage II: acetogenesis

In this stage the acetogenic bacteria consume primary products .In the second step, acidogenesis, another group of microorganisms ferments the break-down products to acetic acid, hydrogen, carbon dioxide and other lower weight simple volatile organic acids like propionic acid and butyric acid which are in turn converted to acetic acid.

Stage III: methanogenesis

This process utilizes two distinct types of methanogenic bacteria. The first reduces carbon dioxide to methane and the second decarboxylates acetic acid to methane and carbon dioxide. [3]

Finally, these acetic acid, hydrogen and carbon dioxide are converted into a mixture of methane and carbon dioxide by the methanogenic bacteria (acetate utilizers like Methanosarcina, Methanothrix, hydrogen and formate utilizing species like Methanobacterium, Methanococcus, etc.

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

$CH_3COOH \rightarrow CH_4 + CO_2$

2. MATERIALS REQUIRED

- Oil cake (substrate)-
- Anaerobic sludge (Inoculums)
- Batch reactor
- Heat exchanger
- Agitator (for continuous stirring)

2.1. Oil cake

Oil cake is a by-product from oil. After the oil is extracted from oil seeds, the remaining residue is called as oil cake. This oil cake acts as a substrate and food to bacteria's to survive and achieve higher efficiency rate in reduction of green house gases.

2.2. Sludge

Sludge is an inoculums which generates microorganisms. Thereby the microbes feed on substrate to produce gas. Digested waste sludge from domestic waste treatment plant is used. Sludge is to be kept out of contact from oxygen and thickened before using. Sludge with oil cake is therefore purged with nitrogen to allow oxygen escape from the reactor and nitrogen.

2.3. Batch reactor

The Batch reactor is the generic term for a type of vessel widely used in the research fields in anaerobic process. Batch reactor is a simple form of a reactor where the process can be carried out easily with no complex set up. For more efficient process the anaerobic process can also be carried out in a continuous reactor.

2.4. Agitator

Agitator is used for uniform mixing. Since the anaerobic process consists of substrate and inoculum which are non mobile in nature, it is necessary to make contact between both substrate and inoculum an agitator can efficiently mix them together

2.5. Heat exchanger

Anaerobic digestion takes place in mesophilic temperature. Bacterium and microbes need 30 - 50^{0}C temperature for their survival. In UK in order to attain suitable temperature, heat exchangers are used. Here shell and tube single pass counter flow heat exchanger is used to maintain suitable temperature for microbe growth.

3. FACTORS GOVERNING THE PRODUCTION OF BIOGAS YIELD

3.1. pH

pH is a most important factor in the growth of bacteria and microbes. pH of the digester should be maintained 6.9-7.2 by feeding them properly. If the pH level increases the whole system will become toxic, if it lowers the microbes will die.

3.2. C/N (carbon/ nitrogen) ratio

It is necessary to maintain proper composition of the feedstock for efficient plant operation so that the C: N ratio in feed remains within the limit. It is generally found that during anaerobic digestion microorganisms utilize carbon 25-30 times faster than nitrogen. To meet this desired requirement, microbes need a 30:1 ratio of C to N with the largest percentage of the carbon being readily degradable. Waste material has carbon can be combined with materials high in N to attain desired C: N ration of 30:1 [6]

3.3. Mixing

Stirring of digester contents needs to be done to ensure intimate contact microorganisms and substrate which ultimately results in improved digestion process. Agitation of digester contents can carry out in a number of ways. For instance daily feeding of slurry instead of periodical gives the desired mixing effect. Mild mixing also evolves gas, providing mixing should be carried out carefully, making sure that the substrate and sludge do not stick on the sides of the reactor [6].

3.4. Particle size

Particle size is another most important factor to consider before starting up the process. The biogas production deals with bacteria's of nanosize, so the feed material must be fine. Otherwise it would be difficult for bacteria's to carry out digestion. Smaller the particle (50-250nm) larger the surface area of adsorbing, so that would increased in microbial activity and increased in gas production. [6]

3.5. Effects of nutrients

The presence of ions in the feed is critical parameter, since it affects the whole process. The bacterias in digestion process were nano-metric size, it requires micronutrients and elements like nitrogen, phospjorus, calcium, magnesium, cobalt, nickel, zinc, manganese and copper for their growth. Although these elements are needed in extremely low concentrations (nanometers to micrometers)

3.6. Total solids

Total solid is a term applied to the material residue left in the vessel after evaporation of the sample and its subsequent drying in an oven at the defined temperature. The sample is grounded well manually and taken in a silica crucible and is heated in an oven for an hour at 100^0 C. Then the pre heated sample is taken out and placed in a desiccators containing calcium which absorbs heat without allowing moisture from air and then weighed yielding total solids. Moisture content of oil cake was found to be 42 %

3.7. Volatile solid measurement

Fixed solid is the term applied to the residue of the total, suspended or dissolved solids after ignition for a specified time at the specified temperature. The weight loss on ignition is called volatile solids. Determination of fixed and volatile solids do not distinguish precisely between organic and inorganic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. [10] Sample which is weighed from the oven, is placed in a furnace for 1 hour at 550^0C and allowed to cool in the furnace for 5 hours and then placed in a desiccators and weighed.

Moisture content %	Ash content %	Total dry solids (vs) %
42.62%	36.5%	61.29 %
32.81 %	36.76 %	61.48%
34.68 %	37.16 %	61.79 %

From the experimentation volatile solids of substrate and volatile solids in sludge were calculates, based on this calculation F/M ratio was calculated. F/M ratio depends on the amount of volatile substances present in substrate and inoculums, which needs to degrade to produce biogas during mechanism.

3.8. Chemical oxygen demand (COD)

The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time. 10ml of sludge is taken along with one spatula of mercuric suplhate added with 2.5 grams of oil cake and 1.5 ml of potassium dichromate. Then 3.5 ml of sulphuric acid is added and the sample is heated for 2 hours, cooled and titrated against Ferrous Ammonium Sulphate (FAS) using ferroin indicator and the end point appearance should be dark red color. COD is found to be 755.53mg/l

4. EXPERIMENTAL SETUP

Two reactor bottles, One containing water is placed upside down supported by a stand and the other containing substrate + inoculum at its side, both reactor are closed tightly with a rubber cork. A tube with syringe needles at its end is used to connect the two reactors by inserting the needle inside the rubber cork of the reactor. Another needle with an open end is inserted into the reactor containing water, through its cork, and a beaker is placed at its bottom, such that the water droplet from the open end of the needle gets collected inside the beaker. The reactor containing substrate and inoculum should be shaken slowly for the evolution of gas. When the gas is evolved, it travels through the tube, reaches the other reactor, gets collected at the top of the reactor containing water, displacing equal volume of water in the beaker. Volume of the gas evolved was measured by measuring the volume of water displaced from the bottle.

Fig 2: experimental setup

4.1. Sludge activity

Activity of sludge was measured by taking sludge with initial concentration of Sodium acetate solution. The gas production from this process must exceed 500-600ml of gas. Otherwise the sludge is considered to non active, and needs further pre-treatment for microbial growth.

4.2. F/M (Food/ Microbe) ratio

Food microbe ratio or substrate to inoculum ratio is necessary to be calculated in order to achieve correct proportion of reactants mixture since if either of the reactants is taken without correct ratio there will be no production of gas. In other words, F/M ratio is the ratio of volatile solid content of the substrate to volatile solid content of sludge.

Table 1: Biogas produced on F/M ratio

Days	Control 1	F/M =1	F/M =1	F/M =1.25	F/M =1.25	F/M =1.5	F/M =1.5
1	9	7	7	15	12	30	32
2	8	17	20	23	20	52	50
3	11	24	28	40	38	59	63
4	13	26	30	55	62	72	68
5	15	24	28	66	63	72	70
6	19	20	22	68	71	73	75
7	14	18	19	60	66	65	68
8	16	11	17	59	53	66	63
9	11	9	12	53	45	39	43
10	10	8	11	38	32	36	32
11	5	8	10	20	15	21	23
12	5	4	8	13	11	15	13
13	4	3	7	10	10	10	8
14	3	2	5	10	11	5	6
15	-	2	2	8	7	2	3

Above table gives us the data of biogas produced on various days with respect to different concentrations. Control is the volume of gas produced from sludge only, without adding substrate to study the potential of substrate. By using trial and error method, two reactors were setup for each F/M ratio to find average amount of gas produced.

4.3. MASS BALANCE

Input= output+accumulation

Input= oil cake + sludge

Output = biogas

Accumulation= Digestate

Mass balance is based on Volatile Solid (VS) content

Table 2. Volatile Solid of sample after process completion

VS OF THE SAMPLE AFTER THE PROCESS COMPLETION (mg/l)
21032.3
15323.8
10187.5
11232.1

Input

Oilcake

VS (oil cake) = 0.6164g in 1 g of oil cake

Since for the F/M ratio of 1.5 yield maximum volume of gas we consider the ratio 1.5 for mass balance

12.175g of oil cake is taken

So, VS of 12.175g of oil cake = 7.5g

VS of oil cake here = 7.5g

Sludge

5g of VS in 200ml of sludge

Input = oilcake + sludge

= 7.5 + 5

= 12.5g

Accumulation

Digestate = 101875 mg/l

= 1.01875 g VS in 200 ml

Input – output = accumulation

12.5 - output = 2.0375

Output = 10.4625 g

Total gas produced in 12 days = 600 ml

So 10.4625 g of VS is utilised in 12 days to produce 600 ml of biogas

Conversion $(X_A) = \frac{10.4625}{12.5}$ (3)

= 83.7%

Total production of gas produced in 12 days is 600 ml

Conversion is 83.7 %

5. Results and discussions

Biogas can be used for all applications designed for natural gas, subject to some further upgrading as not all gas appliances require gas of with the same quality standards. Biogas can be used to heat boilers. The heat has many applications such as being used in plant for producing water vapour for industrial process. Methane produces 20% more energy than coal. Boilers do not have a high gas quality requirement. It is preferable to remove the hydrogen sulphide because it forms sulphurous acid in condensate which is highly corrosive. It is also recommended to condense the water vapour in raw gas. Water vapour can cause problems in gas nozzles. Removal of water will also remove large proportion of hydrogen sulphide.

Biogas is also used in combined heat and power units.gas engines do have the same quality requirements as boilers, except hydrogen sulphide content which should be lower. In biogas engines which uses NOx, emissions are usually low because of CO_2 in the gas.CO concentration is often more a problem. However from an environmental point of view CO is less of an issue than NO_x because it is rapidly oxidised to CO_2. CHP units are good way to produce efficiently more both electricity and heat for AD plant. For instance heating of the digester and sterilisation of digestate can be done using this heat. The remaining electricity can be sold to national grid. This is actually the most popular way of using the landfill gas

In case of raw biogas, the distance from the plant and the gas user must be taken into account. Indeed the cost of piping the gas can be prohibitive. If no potential users are located in surroundings, the biogas should be on site in CHP unit or upgraded for the use as a vehicle fuel or for distribution of electricity via natural gas grid.

The utilizations of biogas as a fuel for vehicles require the same type of engine as those used for natural gas. However the gas quality demands are strict. Thus biogas can be upgraded to obtain:

- A higher calorific value(for vehicles to operate long distance)
- A consistent gas quality for safe driving and engine operation
- No enhancement of corrosion due high levels of H_2S,NH_3 and water
- A gas without any mechanically damaging particles

In practice it means that methane content should be increased to 95% and the gas should be compressed. Upgraded biogas is considered to be one of the cleanest fuels with minimal impact on environment and human health. Although such operations can involve only on commercial basis.

The methane contained in the biogas can also be used as fuel for fuel cells. Fuel cells are power generating systems that produce DC current by combining fuel and O_2 in an electro chemical reaction. There is no intermediate process. A number of power plants are operated in Japan and USA with electrical efficiency of 41% biogas plants have been set up in Fangel (Denmark) which exclusively sells electricity to grids.[8]

From table 1. Graphs were generated to estimated the production of gas and which F/M ratio was more accurate in maximized gas production.

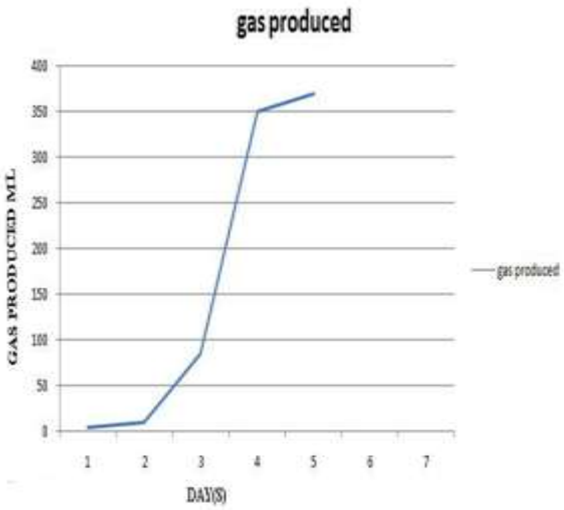

Fig 3: Sludge activity

From fig 3 it is found to be 550 ml of gas was produced and activity of sludge was determined.

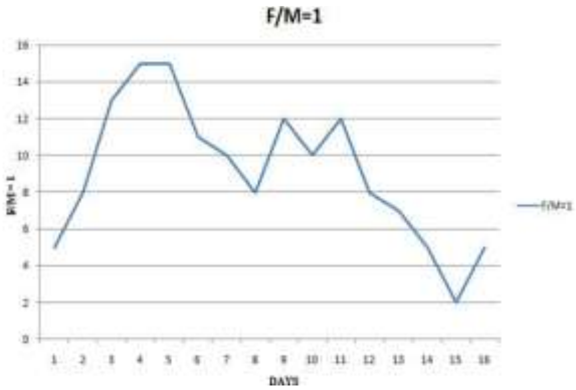

Fig.4: F/M ratio =1

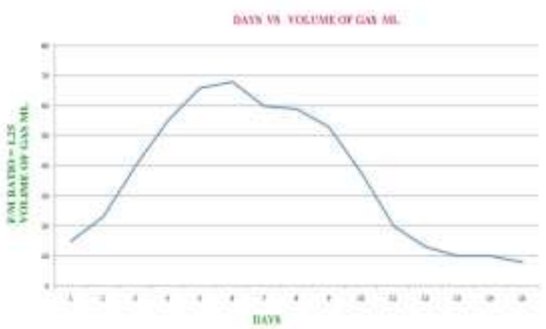

Fig.5: F/M ratio = 1.25

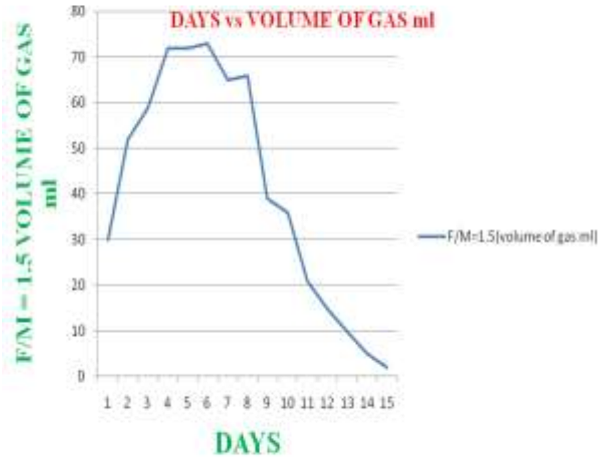

Fig 6. F/M ratio =1.5

Fig 7. F/M ratio vs volume of gas produced based on F/M ratio

Production of biogas is high in F/M = 1.5, higher the ratio greater is the production of gas. The microbial process comprises the main degradation steps such ah hydrolysis, acidogeneis, acetogenesis and methanogenesis (fig 6) the whole process was efficient, balanced and required amount of biogas was produced. It is been observed from above graphs that micoorganisms that are active during the hydrolysis of polysaccharides in biogas processes include various bacteria and anaerobic fungi. During this hydrolysis process extracellular enzymes produced by microorganisms are utilized for degradation of the organic matter present inside the reactor. For an effective biogas production we need to make sure the hydrolysis is efficient. The production of biogas depends on the two main processes that contain varied species of microorganisms that are classified as acideogens and methanogens. The log phase of the graph shows the acetogenesis process where higher VFAs and other intermediates are converted into acetate, with hydrogen also being produced [15]. Stationary phase of the graphs shows the methanogenesis process and most important stage of anaerobic digestion process where intermediates are consumed by methanogenic microorganisms to produce biogas. After the proction of biogas, as nutrients become less available and waste products increase, the number of dying microbes continues to rise and production of biogas starts to drop. It has been observed that the hydrolytic enzyme production was high at initial days of digestion, followed by acidogeneis and acetogenesis in day 3. Methanogeneis process started occurring from day 5 to 9 producing high yield of biogas and started declining afterwards indicating depletion of nutrients in reactor.

The deviation in graph (fig 4, fig 5 and fig 6) shows the acidogenic process and variation in pH. The pH level of the systems were continuously monitored by pH metric electrode, pH variation is well maintained by adding few drops of acetic acid (C_2H_5OH) and sodium acetate (C_2H_3OONa). From the Table 1. data, mass balance was calculated to find out percentage of biogas produced from this process, from equation (3) it was found to be 83.7% approximately 84% of conversion takes place. From this Biogas the possible amount we can generate 0.3Mw to 1Mw of electricity in large scale reactor (digester capacity of one ton). After the conversion process CHNS analysis was carried to determine the chemical potential of digestate [6]. It was found to be

Table 3. CHNS analysis of digestate.

FEED MATERIAL	C%	H%	N%	S%	C/N ratio
Digestate	48.80	6.20	3.85	1.53	12.70

From the above values, the digestate from this anaerobic process can be used as organic manure which is eco-friendly to enrich the soil and increases crop production. However the different factors like substrate composition and quality, temperature, pH and microbial growth contributes the efficiency of this process and optimized to achieve maximum benefit from this bio-nanotechnology in terms of energy production and waste management. By adjusting the parameters like pH, substrate, concentration, C/N ratio we can achieve 90% conversion[5].

6. Conclusions

This technology includes low cost production of clean biogas (a renewable form of energy) from anaerobic microbes. The organic wastes are degraded by these microbes with different concentration of substrate to find efficient percentage of F/M ratio. This technology can be very much helpful for solid waste management as well as vital for meeting future energy-needs. The prime advantages of this technology include

(i) Organic wastes with a low nutrient content can be degraded by co-digesting with different substrates in the anaerobic bioreactors, and
(ii) The process simultaneously leads to low cost production of biogas, which could be vital for meeting future energy-needs.

However, different factors such as substrate and co-substrate composition and quality, environmental factors (temperature, pH, organic loading rate), and microbial dynamics contribute to the efficiency of the anaerobic digestion process, and must be optimized to achieve maximum benefit from this technology in terms of both energy production and organic waste management. Today around 50% of MSW is land filled, with a content of around 30% of organic fractions. Another factor that in the near future will contribute to the consolidation of anaerobic digestion as a mainstream technology for the MSW is the fact that the digested residue can be considered quite stable organic matter with a very slow turnover of several decades given adequate soil conditions. In this way the natural imbalance in CO2 can be adjusted by restoring or creating organic rich soil .The removal of CO2 constitutes an extra benefit that could help place AD among the most relevant technologies in this field.

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