CONVERSION OF HIGH COD CONTENT WASTEWATER INTO BIOGAS

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ABSTRACT

High concentration of COD was observed in the bagasse wash waterused for the production of pulp in the paper manufacturing industry (Tamil Nadu Newsprint and Paper Limited) at Karur. In current scenario the waste water is sent to the Effluent Treatment Plant and the COD is considerably reduced. The production of biogas led to this study in order to obtain sustainable treatment process, the idea of Biomethanation is one of the significant techniques in handling high COD content waste water. Biogas is one of the prime sources of fuel that can be used for fire kilns and power generation. The technique is feasible and sustainable due to its waste management strategy. With an average production of 15000m3 gas per day reduces 40kl of oil being used. Hence this helps in optimum usage of natural resource. The key technique used is the Upflow Anaerobic Sludge Blanket reactor (UASB).

Keywords: *Biogas, biomethanation ,COD ,natural sources, UASB, waste management*

I. INTRODUCTION

1 General

Wastewater can mean different things to different people initially from its generation and the type of treatment. Tamil Nadu Newsprint and Paper Limited (TNPL), located at Kakithapuram, Karur is a paper manufacturing industry . Because of the mass production of pulp using the bagasse that comes as the waste from the sugar manufacturing industry there is an increase in the COD content of the wastewater released . The conversion of that wastewater into biogas has led to a new resource generation operation and also an effective treatment in the reduction of high COD upto 75%. Though the treatment was carried out through the Effluent treatment Plant the efficiency of the COD reduction was not upto the expected level . Biogas is a form of natural fuel at very low cost. The installation of biogas plant is high but the biogas cost per m3 is low range for this industry.

The industry has various process like soda recovery , lime kiln and many number of boilers. All these boilers was using furnace oil which is 15 times costlier than the biogas. It is also highly dangerous to store the furnace oil. The monthly usage of the oil in the industry is about 150kl but by the production of biogas this can be reduced by 70%. Hence cost of purchasing and maintenance is considerably reduced and stress on the natural resource is being reduced to the maximum extent. The production of biogas requires anaerobic condition.

The production of methane using microorganisms in the absence of oxygen is known as the biomethanation. This can be achieved using a UASB reactor.

The raw effluent produced from the process of bagasse washing and cooking is around 6500-7500 m3 per day. This raw effluent is sent to further process and finally obtain the biogas. The obtained biogas is stored in a gas holder and then sent to the boilers or for power generation. By this way the energy is being used efficiently.

2 COD and its Importance

Chemical oxygen demand (COD) is the total amount of oxygen required to chemically oxidize the bio degradable and non-bio degradable organic matter. It is expressed in milligrams per litre (mg/l) also referred to as ppm (parts per million), which indicates the mass of oxygen consumed per litre of solution. Higher COD levels mean a greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen (DO) levels.

3 Bagasse

Humans Bagasse is a by-product of sugar milling and important fuel resource for that industry. It is a fibrous, low density material with a very wide range of particle sizes and high moisture content. Sugar milling operation of sugarcane gives bagasse which has 45-50% moisture content and consisting of a mixture of hard fibre, with soft and smooth parenchymatous (pith) tissue with high hygroscopic property.

The use of bagasse for paper production must be encouraged to conserve forests. For a bamboo, softwood and other materials had been the traditional fibrous raw materials in the paper industry. But due to global shortage of these raw materials, the paper industry had been exploring the possibilities of using alternate fibrous raw materials, particularly agricultural residues like bagasse

Bagasse is a fibrous residue left after the sugarcane is crushed in the sugar factories for extraction of juice

- 48-50% moisture
- 48% fibre
- 2-4% sugar
- 45% cellulose
- 28% pentosans
- 20% lignin
- 5% sugar
- 2% minerals

II. METHODOLOGY

1. Methodology

Collection of sample

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Analysis of five tank sample

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Analysis of inlet raw effluent and

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Study on daily gas production

Fig 1 Flow chart for Methodology

2 Sample Collection

Sample was collected in the Conical flask and stored at room temperature.

- Raw Effluent
- Clarifier tank
- Buffer tank
- UASB Reactor A
- UASB Reactor B.

3 Testing Procedure

The materials required for the testing are as follows,

- pH meter,
- Muffle furnace.
- Conical flask,
- Test tube
- Funnel,
- Weighing balance,
- Spatula, Filter paper
- , Beaker,
- measuring jar

Fig 2 Raw sample collections

3.1 COD Test

3.1.1 Reagent required

- Pottasium di Chromate ($K_2Cr_2O_7$)
- Mercuric sulphate ($HgSO_4$)
- Silver sulphate ($AgSO_4$)
- N of FAS (Ferrous Ammonium Sulphate)
- Con.Sulphuric acid (H_2SO_4) and
- Ferrion indicator.

3.1.2 Reagent Preparation of 0.1N FAS Solution

39.2 g FAS is dissolved in demineralized water. 20ml Con. Sulphuric acid is added and make up to 1000ml.

Fig 3 COD test

3.1.3 Procedure

To take 5ml of effluent sample and make upto 100 ml in conical flask. 20ml of diluted sample is transferred to a flat bottom of flask. Add a pinch of mercuric sulphate,10 ml of 0.25N $K_2Cr_2O_7$ and a pinch of silver sulphate into the flask . Finally, add 30ml of Con.H_2 SO_4 and heat for 2hrs in 80^oC.

Then add 80ml of demineralized water and cool it, add ferroin indicator. Titrate the solution with 0.1N FAS. Wine red colour appears is the end point. The burette reading is recorded.

3.2 VFA's Test

3.2.1 Reagent required

- Hydrochloric acid (HCl) Solution 0.1N
- Sodium hydroxide solution (NaOH) 0.1N

3.2.2 Scope

The intermediate product of anaerobic biodegradation are VFA's (acetic, propionic and butyric acids). It is necessary to measure VFA content in anaerobic reactors because if these acid are not completely converted to methane, accumulation may occur causing drop in systems pH. Bicarbonate alkanity is buffering capacity of wastewater to neutralize these acids.

Fig 4 VFA's test

3.2.3 Procedure

- 5 samples are taken from inlet and outlet and made upto 100 ml in a conical flask. Add 0.1N HCl into the sample and titrate till it reduces to pH 3.0.

- Note the each sample burette reading. Then, boil the solution for 3 minutes and cool it rapidly.

- Titrate it with 0.1N sodium hydroxide solution . Bring the pH of the solution upto 6.5. Note down the burette readings.

Fig 5 Heating mantle

3.2.4 Importance of test

- It is highly important to study the parameters like COD , VFA , TSS because each thing has connection with the production of gas .
- When COD is high the gas production will also be high .
- Meanwhile the volatile fatty acids should be as low as possible for high gas production .
- TSS helps in determining the sludge content in tanks .

Fig 6 Muffle furnace

4. Process Description

4.1 Bagasse Clarifier

Clarifiersare settling tanks built with mechanical means for continuous removal of solids being deposited by sedimentation. A clarifier is generally used to remove solid particulates or suspended solids from liquid for clarification and (or) thickening.

Concentrated impurities, discharged from the bottom of the tank are known as sludge, while the particles that float to the surface of the liquid are called scum.

In the bagasse clarifier, the bagasse wash water and bleach water are the source of wastewater. In context with paper industry Clarifier removes the bagasse and suspended solids.

4.2 Equalization Tank

Effluent is send to the equalization tank from bagasse clarifier. Equalization is the best means of stabilization of pH. Because of further treatment becomes unless the character is uniform. To accelerate the stabilization process we have installed a aerator to mix the effluent properly. Equalization is the one of the pre-treatment process.

4.2.1Benefits

- Equalization improves sedimentation efficiency by improving hydraulic detention time.

- The efficiency of a biological process can be increased because of uniform flow characteristics and minimization of the impact of shock loads and toxins during operation.

- Treatability of the wastewater is improved and some BOD reduction and odour removal is provided if aeration is used for mixing in the equalization basin.

4.3 Neutralization Tank

Neutralization is the process of adjusting the pH of water through the addition of an acid or a base, depending on the target pH and process requirements

Fig. 2.7 Neutralization tank.

Effluent contains pH around 3-4.5 (bagasse and pulp effluent). So it is to be altered for methanogenic activation (pH value ranging 6.5- 7.5). Milk of lime which comes from the Soda Recovery Plantcausticizer is added to the neutralization tank in order to maintain the pH value.

4.4 Primary Clarifier

The primary clarifiers remove the large suspended solids which are settled at the bottom by centrifugal force, prior to discharge of clear effluent the anaerobic reactor. This significantly reduces the reactor and increases efficiency.Clarifier is used for removing the sand present in the lime . The lime contains calcium content and also the suspended solids that should be removed before the introduction of effluent into the buffer tank .

Fig. 2.8 Primary clarifier

4.5 Buffer tank

The aim of a buffer is to realise a consistent volume and possibly a consistent quality. It is implemented to allow further purification processes to run as effectively as possible. The buffer can be in-line or off-line. In-line buffering involves the entire quantity of wastewater flowing through the buffer tank. In off-line buffering, only part of the wastewater flows into the buffer tank at specific moments.

In principle, the buffer tanks feature a level-measure and a mixer- stirrer to realise a good mix (or buffering). It is used for equalization of the inlet volume and temporary treatment of peak loads.The term buffer means neutral . The tank is designed based on COD , organic load . If high load is sent to the UASB reactor then the efficiency lacks hence it is mandatory to reduce the organic loading .

5.Upflow Anaerobic Sludge Blanket (UASB) Process

5.1 Working Principle

Industrial wastewater flows into the bottom of an anaerobicupflow tank. Accumulated sludge forms granules. Microorganisms living in the granules degrade organic pollutants by anaerobic digestion. The sludge blanket is kept in suspension by the flow regime and formed gas bubbles. A separator at the top of the reactor allows to recover biogas for energy production.

5.2 Design Consideration

UASB Reactors are constructed out of concrete or another watertight material and can be designed in a circular or rectangular way. Critical elements for the design of UASB reactors are the influent distribution system, the gas-solids separator, and the effluent withdrawal design. The gas that rises to the top is collected in a gas collection dome and can be used as energy (see also use of biogas) for cooking, heating or other, but scrubbing before use is required. If the biogas is converted to electricity, the heat produced as a by-product can be reused to heat the reactor, favoring anaerobic digestion.

To maintain the reactor well-mixed and allowing the formation of granules and a good contact of the active sludge blanket and the influent sewage, it is critical that the influent is equally distributed in the bottom before moving upwards.Besides these design requirements, the main influencing parameters are pH, temperature, chemical oxygen demand (COD), volumetric COD loads, HRT and flow, upflow velocity, concentration of ammonia and start-up phase.

5.3 Hydraulic Retention Time(HRT)

The hydraulic retention time (HRT) should not be less than 2 hours. Anaerobic microorganisms, especially methane producing bacteria, have a slow growth rate. At lower HRTs, the possibility of washout of biomass is more prominent. The optimal HRT generally lies within 2 to 20 hours

5.4 pH control

The pH-value needs to be between 6.3 and 7.85 to allow bacteria responsible for anaerobic digestion to grow. The pH-value is also important because at high pH-values, ammoniac (NH_4+) dissociates to NH_3 which inhibits the growth of the methane producing bacteria.

5.5 Temperature

For an optimal growth of these bacteria and thus a optimal anaerobic digestion, the temperature should lie between 35 to 38°C. Below this range, the digestion rate decreases by about 11% for each 1°C temperature decrease and below 15°C the process is no longer efficient, although bacterial activity can still be noticed at temperatures less than 10°C.

5.6 COD Loads

Influents should have concentrations of above 250 mg/L COD, as for lower rates, anaerobic digestion is not

beneficial. Optimum influent concentrations are above 400 mg/L COD and an upper limit is not known.

Fig.10 UASB reactor

5.7 Upflow Velocity

The upflow velocity in UASB is an important design parameter as the process plays with the balance of sedimentation and upflow. On one hand, sludge should not be washed out the reactor, and on the other hand, a minimum speed needs to be maintained to keep the blanket in suspension, and also for mixing. An upflow velocity of 0.7 to 1 m/h must be maintained to keep the sludge blanket in suspension. Primary settling is usually not required before the UASB.

6 Process of Stages

The anaerobic degradation of complex matter is carried out by a series of bacteria. There exists a coordinated interaction among these microbes. The process may fail if certain of these organisms are inhibited.

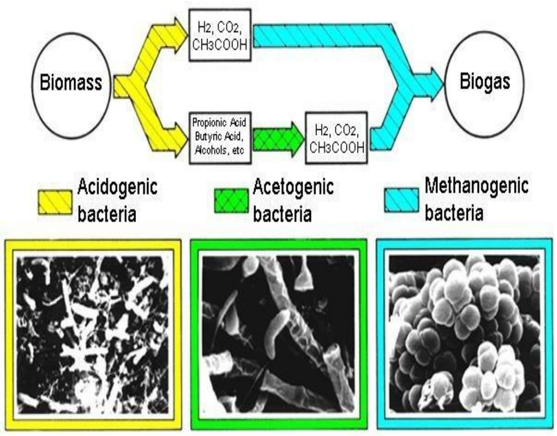

Fig 11 Microbial process in UASB reactor

6.1 Hydrolysis

During hydrolysis, the first stage, bacteria (i.e, Fermentative bacteria or hydrolytic bacteria like as Bacillus, Cellulomonas and Eubacterium.) transform the particulate organic substrate into liquefied monomers and polymers i.e. proteins, carbohydrates and fats are transformed to amino acids, monosaccharides and fatty acids respectively. Equation1 shows an example of a hydrolysis reaction where organic waste is broken down into a simple sugar, in this case, glucose.

$C_6H_{10}O_5 + 2H_2 \rightarrow C_6H_{12}O_6 + 2H_2$ Eqn1

6.2 Acidogenesis

In the second stage, acidogenic bacteria (Propionibacterium, Butyrivibrio, Acetivibrio) transform the products of the first reaction into short chain volatile acids, ketones, alcohols, hydrogen and carbon dioxide. The principal acidogenesis stage products are propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), acetic acid

(CH_3COOH), formic acid ($HCOOH$), lactic acid ($C_3H_6O_3$), ethanol (C_2H_5OH) and methanol (CH_3OH), among other. From these products, the hydrogen, carbon dioxide and acetic acid will skip the third stage, acetogenesis, and be utilized directly by the methanogenic bacteria in the final stage. The following equations represent three typical acidogenesis reactions where glucose is converted to ethanol, propionate and acetic acid, respectively.

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \qquad \text{Eqn2}$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \qquad \text{Eqn3}$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COO \qquad \text{Eqn4}$$

6.3 Acetogenesis

In the third stage, known as acetogenesis, the rest of the acidogenesis products, i.e. the propionic acid, butyric acid and alcohols are transformed by acetogenic bacteria (i.e, Clostridia and Acetivibrio) into hydrogen, carbon dioxide and acetic acid. Hydrogen plays an important intermediary role in this process, as the reaction will only occur if the hydrogen partial pressure is low enough to thermodynamically allow the conversion of all the acids.

Equation 5 represents the conversion of propionate to acetate, only achievable at low hydrogen pressure. Glucose Equation 6 and ethanol Equation 7 among others are also converted to acetate during the third stage of anaerobic fermentation.

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2 \qquad \text{Eqn5}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \qquad \text{Eqn6}$$

$$CH_3CH_2OH + 2H_2O \rightarrow CH_3COO^- + 2H_2 + H^+ \qquad \text{Eqn7}$$

6.4 Methanogenesis

The fourth and final stage is called methanogenesis. During this stage, microorganisms convert the hydrogen and acetic acid formed by the acid formers to methane gas and carbon dioxide. The bacteria responsible for this conversion are called methanogens and are strict anaerobes. Waste stabilization is accomplished when methane gas and carbon dioxide are produced.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{Eqn8}$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \qquad \text{Eqn9}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{Eqn10}$$

III. RESULT AND DISCSSION

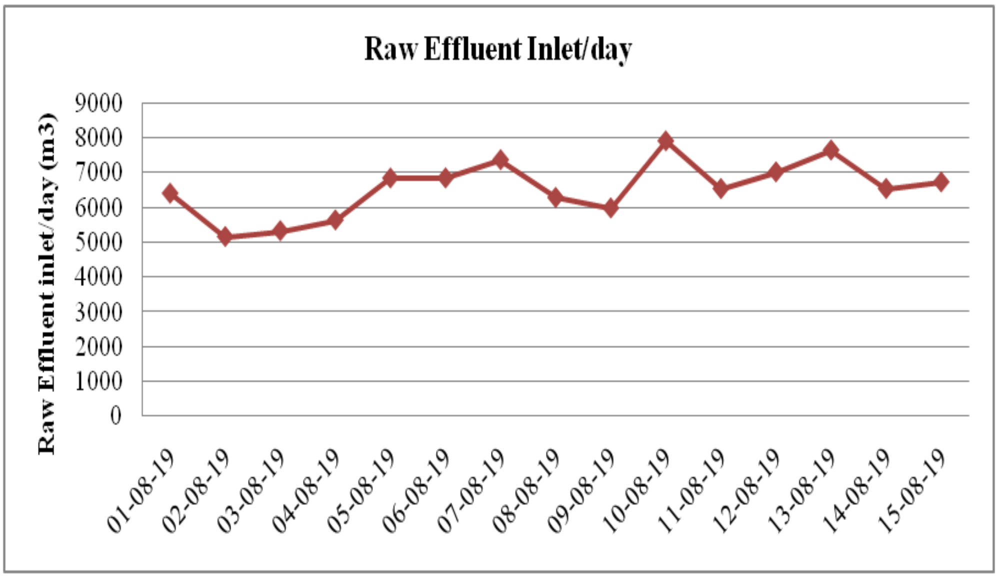

Fig 13 Raw Effluent Inlet/day

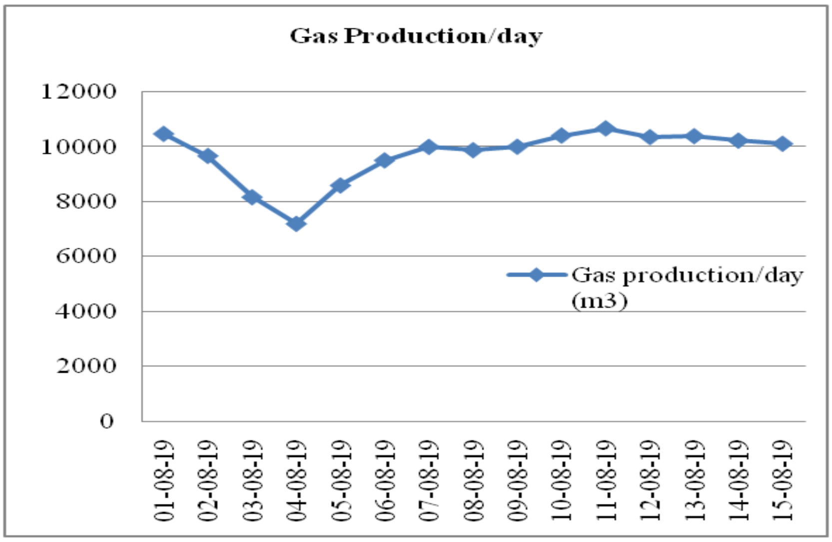

Fig 14 Gas production per day

IV. CONCLUSION

In present scenario most of the paper industries are using bagasse as an alternate for wood in the production of pulp. Hence the production of biogas is feasible in all the units. By the production of biogas, the stress on the natural resources like oil and coal are reduced to a greater extent. Also the presence of bacterial dead cells makes low production of biogas. So, in order to reduce the dead cells of bacteria, cow dung is used as feed and this decreases the bacterial dead cells simultaneously and increases the methanogenic activity. Hence this technique can be used effectively.

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