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Optimization of Biomethanation Process for High TDS Spent Wash from Distilleries

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Abstract- The Production of ethanol in distilleries based on cane-sugar molasses constitutes a major industry in the several countries in the world. The world's total production of alcohol from molasses is more than13 million m^3/annum. The aqueous distillery effluent stream known as spent wash is a dark brown highly organic effluent and is an approximately 12-15 times by volume of the product alcohol. It is one of the most complex constituent and strongest organic industrial effluents, having extremely high COD and BOD values. Because of the high concentration of organic substituent, distillery spent wash is a potential source of renewable energy. The technologies presently used by distilleries for treatment of waste are Biomethanation followed by a two stage biological treatment and disposal in water courses or for utilization on land for irrigation or for compositing with or without biomethanation and concentration and incineration. These technologies have their own limitations. Anaerobic digestion of Biomethanation waste, like spent wash, result both energy generation which reduces green house gases and replaces the use of fossil fuels. The use of methane from the waste is not a new technology. The method followed losses lot of energy in the form of methane gas. This is also of national priority. The present work is 'an attempt to provide suitable microbes and a process for Biomethanation even with high TDS spent wash.

Keywords: Molasses,Spent wash, Biomethanation, anaerobic digestion,fossil fuels**.**

1. INTRODUCTION

The spent wash is a beneficial by product obtained from distilleries after extraction of alcohol from molasses. It is a plant extract derived from sugar cane and contains nutrients and easily oxidisable organic matters. Spent wash is a rich source of organic matters and Nutrients like nitrogen, phosphorous, potassium, calcium and sulphur. In addition, it contains sufficient micronutrients such as iron, zinc, copper, manganese boron and molybdenum. It does not contain any toxic heavy metals and hazardous constituents. It also increased the soil fertility to increase’s the yield. Since the spent wash are having a lot of organic inputs. It is used for biomethanation (biogas generation), the technologies presently used by distilleries for treatment of wastewater are biomethanation followed by a two 'stage biological treatment and disposal in water courses or for utilization on land for irrigation or for compositing with or without biomethanation and concentration and incineration. These technologies have their limitation.

Anaerobic digestion of Biomethanation wastes, like spent wash, result in both energy generation which reduces green house gases and replaces the use of fossil fuels. The use of methane from the waste is not a new technology. The method followed losses lot of energy in the form of methane gas. This is also of national priority. The present work is an attempt to provide suitable microbes and a process for Biomethanation even with high TDS spent wash.

About 295 distilleries in India produce 2.7 billion liters of alcohol and generating 40 billion liters of wastewater annually. The enormous distillery wastewater has potential to produce 1100 million cubic meters of biogas. The population equivalent of distillery wastewater based on BOD has been reported to be as high as 6.2 billion which means that contribution of distillery waste in India to organic pollution is approximately seven times more than the entire Indian population. The wastewater from distilleries, major portion of which is spent wash, is nearly 12-15 times the total alcohol production. This massive Quantity, approximately 40 billion liters of effluent, if disposed untreated can cause considerable stress on the water courses leading to widespread damage to aquatic life.

2. MATERIALS AND METHODOLOGY

The experiments are performed on an Anaerobic digestion is a multi- step biological process where the organic carbon is converted to its most oxidized (CO_2) and most reduced (CH_4) state. The main product of the process is methane which is a mixture of methane and carbon dioxide, as well as traces gases such as hydrogen sulphide and hydrogen. The process involves several groups of microorganisms which makes it complex and sensitive and makes it a valid subject for control and optimization.

Biomethanation is a biological process of generating methane from organic matter mediated by microorganisms. There are three distinct groups of microorganisms involved in the process of Biomethanation and grouped as: Hydrolytic Fermentative Bacteria, Acetogenic fermentative bacteria and Methanogenic fermentative bacteria, the first group comprises Hydrolytic Fermenting Bacteria which perfo1m hydrolysis and acetogenesis resulting in the fo1mation of volatile fatty acids (VFA) and some carbon dioxide and hydrogen. The microorganisms belonging to this groups are *Bacillus, Micrococcus, Clostridium, Vibrio,Peptococcus* .

Acetogenic Fermenting Bacteria constitute the second group and responsible for the oxidation of organic acids, alcohols, and the VFAs with more than two C toms to acetate. In addition, hydrogen, carbon dioxide is also produced during cytogenesis. The microorganisms belonging to this groups ate *Pseudomonas, Lactobacillus, Streptococcus, Escherichia coli Bacteriodes, Ruminicoccus, Butyribacterium, Eubacterium, Propionibacteriuni,*

The third group involves Methanogenic Fermentative Bacteria which convert acetate or carbon dioxide and hydrogen into methane. It is important to note that methane bacteria are strictly anaerobic. The microorganisms belonging to this group are *Methanobacterium Methanococcus, Methanospirillum and Methanosarcina.*

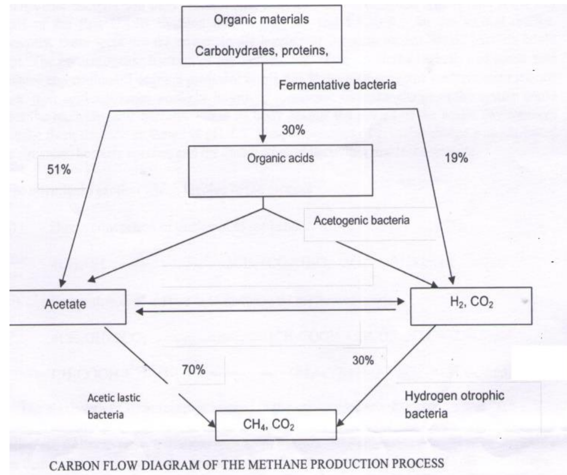


Figure 1. Flow chart of methane production

The chemical reaction which involve in the process

i) Direct conversion of methanol to methane :

$$4\,CH_4 \longrightarrow 3CH_4 + CO_2 + H_2O; \quad \Delta G = -312 \text{ kJ/mol}$$

ii) Fermentation of acetate in to methane by methaogenesis:

$$CH_4OH + 2CO_2 \longrightarrow 3CH_3COOH + 2H_2O; \quad \Delta G = -2.9 \text{ kJ/mol}$$

$$3CH_3COOH + 2H_2O \longrightarrow CH_4 + CO_2 + H_2O; \quad \Delta G = -31.20 \text{kJ/mol}$$

In this study, the two-stage up flow anaerobic sludge blanket (UASB) system and batch experiments were employed to evaluate the performance of anaerobic digestion for the treatment of high concentration methanol waste water. The acid resistance of granular sludge and methanogenic bacteria and their metabolizing activity were investigated. The performance of granular, sludge was attributed to its structure, bacteria species, and the distribution of bacterium inside the granule.

2.1 Characteristics of Spent Wash

Distillery spent wash is highly polluting due to the presence of high concentration of organic matter and inorganic salts. It consists of high Biological Oxygen Demand (BOD-: 5000- 8000 mg/l).Chemical Oxygen Demand (COD: 25000-

30000mg/l). Undesirable foul smell and color. Discharge of raw spent wash in to open land or nearby water bodies resulting in environmental, water and soil pollution including threat to plant and animal lives. Hence Discharge of spent wash is a serious problem.

. But spent wash contains highest content of organic nitrogen and nutrients. By installing Biomethanation plant in distilleries reduces the COD and also increases the nutrient content. This biomethanated spent wash improve the physical and chemical properties of the soil and further increased soil micro flora soil fertility to yield crop productivity.

The waste water generated from bio-still based distillery, the average characteristics are given in the table:

Table 1: Average characteristics of wastewater generated from bio-still based distillery

Parameters	Concentration			
Column - 1	Column – 2	Column -3	Column - 4	Column - 5
	Spent wash generation 1:15 liters	Spent wash generation 1:10 liters	Spent wash generation 1:4 liters	Biomethanation of 4^{th} column
Odor	jaggery	jaggery	jaggery	jaggery
Color	Dark brown	Dark brown	Dark brown	Dark brown
P^H	4.3-4.5	4.0-4.5	4.0-5.0	7.3-7.5
COD	80000-90000	250000-275000	120000-160000	50000-55000
BOD	40000-45000	85000-95000	80000-95000	5500-6000
Total solids	80000-90000	40000-50000	150000-180000	66000-70300
Chloride	5000-6000	5000-6000	10000-12000	5300-5800
Suphate	2000-3000	4000-5000	6000-8000	280-310
Total nitrogen	1000-1200	8000-9000	8000-9000	1200-1340
Potassium	8000-12000	20000-25000	20000-25000	8400-8900
Sodium	2000-3000	2000-2500	2000-2500	230-270
Phosphorus	800-1200	2000-2500	2000-4000	900-1050
temperature	70-80^0c	70-80^0c	70-80^0c	32-35^0c

(*All valu es, other than pH and temperature are in mg/liter unless otherwise stated)

3. RESULTS AND DISCUSSIONS

The maximum COD volumetric loading in the two-stage anaerobic process was 26.8 kg/(m3,d), which was higher than in the one-stage process. Moreover, the system's operating stability and ability to resist impulsive loading in the two stage anaerobic process were obviously better than in the one stage. In the well digesting two stage system, the system's pH was always lower than 6.0 because of methanol fermentation. The pH of the first UASB ranged from 4.9 to 5.8, and the pH of the second reactor ranged from 5.5 to 6.2, which were lower than the pH levels in other studies. The methanogenic bacteria had good performance in resisting an acidic environment. They degraded organic matter at a high rate when the pH was between 5.5 and 6.0. Even at pH 5.0 the bacteria could still maintain a steady metabolizing capacity. The adaptability of the methanogenic bacteria existing in the granular sludge was stronger than in dispersive status themselves. At pH 4.5, the anaerobic granule sludge could still degrade organic matter because of the structure characteristics and microbiological community. The methanogenic bacteria metabolized more actively when the pH was above 5.5.

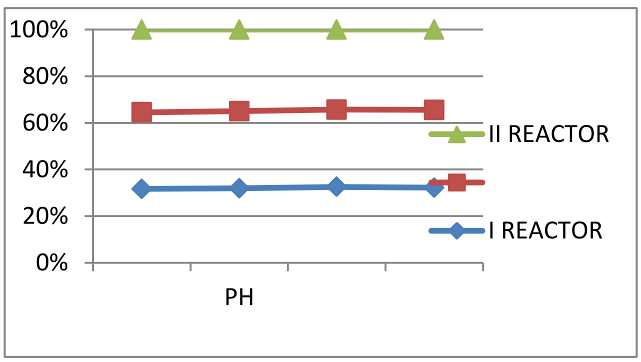
The results show that the pH of the first UASB changed from 4.9 to 5.8 and5.5 to 6.2 for the second reactor. Apparently, these were not the advisable pH levels that common methanogenic bacteria could accept. The methanogenic bacteria of the system, viz. Methanosarcina barkeri, had some acid resistance and could still degrade methanol at pH 5.0.

If the methanogenic bacteria were trained further, their acid resistance would be improved somewhat. Granular sludge of the system could protect the methanogenic bacteria within its body against the impact of the acidic environment and make them degrade methanol at pH 4.5.

Present work is an attempt to provide suitable microbes and a process for biomethanation with even high TDS spent wash:

Table.2. pH values of the batch experiment.

Batch Experiments	Reactor-1		Reactor-2	
pH	4.9	5.1	5.5	5.6
	5.1	5.3	5.6	5.8
	5.5	5.6	5.8	6.0
	5.6	5.8	6.0	6.2



Graph.1. Variation of pH

4. CONCLUSION

Spent wash is a useful resource even though it is a byproduct of distilleries. It must be treated in a proper manner to be discarded into the environment. Biomethanation is the process in which spent wash is treated to produce methane and in parallel to reduce COD, BOD and pH. This process enables the industries to gain energy in terms of methane gas for heating and generating electricity.

The spent wash thus treated can be sprayed on mud to get composited press mud which can be used as bio-fertilizer. Hence making this technique dually beneficial and a zero pollution method.

Anaerobic digestion is a complex process and sensitive to changes in environment conditions. A good online monitoring should be based on reliable indicators. It control and consequently improve the better economy of the biogas plants. The system should be robust with low maintenance requirement and low cost compared to the total investment and operating costs of the plant. The on line information can also be an excellent aid to support decision making and problem solving for the plant operators.

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