Anaerobic Digestion of Vinasse for the Production Of Methane in the Sugar Cane Distillery

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Abstract

The expansion and diversification of new alternative energy sources in a sustainable and efficient way figures strongly among the major concerns of the industrialized world. Recent energy supply crunches and price spikes have propelled ethanol as an alternative transportation fuel. Ethanol derived from renewable sources has brought a host of challenges along with opportunities to the sugar industry. Providing cost effective systems for the treatment, conservation and recycling of water and energy resources is definitively one of these challenges.

Vinasse, the liquid residue left in the distillation of ethanol from sugar cane derivates, frequently poses serious disposal challenges as evidenced by its high biochemical oxygen demand (BOD). On an average basis, 12 cu ft of vinasse per cu ft of ethanol are produced in the distillery, with a BOD load ranging from 1.06 to 3.12 lb/cu ft of vinasse (17,000 to 50,000 mg/l). A study was carried out to assess the anaerobic digestion of vinasse for the production of methane. The purpose of this study was to gather enough data for subsequent evaluation of the technical feasibility of the process. The anaerobic digestion featured a complete mix reactor (digester) utilizing a two steps acid and methane-producing bacteria (thermophilic). Calculations data included temperature of 40ºC (104ºF) and mean cell residence time of 10 days. Results of a mathematical anaerobic digestion model (MADM) built to evaluate the system indicated that a 90% BOD reduction in the vinasse could be obtained by anaerobic digestion in a sugarcane-to-ethanol distillery producing 1,500,000 cu ft per year of ethanol (38,000,000 l per year).

As a byproduct of the digestion process, methane (CH_4) and other gases are produced in quantity enough to generate 3.6 to 10.60 megawatt of electricity (assuming 90% thermal efficiency), when vinasse BOD ranged from 1.06 to 3.12 lb/cu ft, respectively (17,000 to 50,000 mg/l). The gas production per weight of BOD destroyed was 8.92 cu ft/lb, while the food to microorganism (F/M) was 31.03 lb BOD/lb cell mass. In addition, daily production of cellular mass ranged from 3,658 to 10,758 lb/day (for a yearly operation of 150 days) when vinasse BOD ranged from 1.06 to 3.12 lb/cu ft (17,000 to 50,000 mg/l). The volume of the digester ranged from 1,048,836 to

440,857 cu ft (29,697 to 12,482 kl) when vinasse BOD ranged from 1.06 to 3.12 lb/cu ft (17,000 to 50,000 mg/l). Calculated data indicate that the productivity ratio of methane-vinasse ranged from 5.11 to 15.03 cu ft of methane per cu ft of vinasse digested and that of methane-ethanol ranged from 61.31 to 180.32 cu ft of methane per cu ft of ethanol.

Introduction

At the turn of the 20th Century, energy supply crunches and price spikes focused attention on the need for industrial process improvement and development of alternative energy sources such as ethanol fuel (Renewable Fuel Association, 2004). Recent breakthroughs in enzyme technology and processing are radically changing the viability of ethanol as a transportation fuel. However, pressing economical constraints and environmental regulations have placed a demand for increased productivity and diversification of the industrial plant byproducts portfolio. Segregating the less valuable fractions for use as fuel, thus creating value-added products, appeals to present productivity demands. Sugar cane distillery waste disposal improvements are strongly needed, as evidenced by vinasse, or stillage, which is the liquid residue left after distillation of alcohol.

The average production of vinasse in the sugarcane distillery is approximately 12 gallons of vinasse per gallon of ethanol, which represents an enormous volume of wastewater for disposal. When evaluated in population terms or a per capita basis, a distillery with a daily production of 110,000 gallons of ethanol is equivalent to wastewater production for a city with a population of approximately 768,000 people. However, it is not necessarily the volume of vinasse but restrictions for effluent's biochemical oxygen demand (BOD) discharge by current environmental laws and regulations that seems to present the biggest challenge to the profitable use and disposal of vinasse.

Among available technology, anaerobic digestion is one of the dominant BOD reducing processes in wastewater treatment, since gas of high calorific value is produced, as well as relatively inoffensive sludge suitable for use as a fertilizer. A mathematical anaerobic digestion model (MADM) was developed to evaluate the anaerobic digestion of the vinasse as a way of improving the sugar-to-ethanol distillery productivity.

The purpose of the MADM was to gather enough data for subsequent evaluation of the technical feasibility of vinasse anaerobic digestion. Data gathering included key design parameters for the process of anaerobic digestion, such as digester or reactor volume, mass of cellular tissue, total volume of gas produced, as well as the electrical power capabilities of the gas produced.
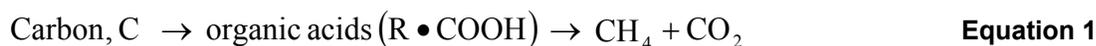
Since the design of anaerobic digestion processes is based on fundamental principles of microbiology, biochemistry and kinetics engineering, the scope of this study will present (1) a background overview of microbiological and biochemical process fundamentals governing biological growth and waste treatment kinetics (2) a brief description of vinasse itself, (3) a description of the methodology used in the development of the MADM, (4) results of the mathematical model (MADM) output (5) discussions of results and (6) conclusions.

Background

Microbiological and Biochemical Overview

Anaerobic treatment can be defined biochemically as the conversion of organic compounds into carbon dioxide, methane and microbial cells (sludge), in the absence of free or molecular oxygen (Corbitt, 1989). For anaerobic treatment of organic nitrogen compounds, the end products will also include ammonia (Appendix A, equation A- 2).

The oxidation and reduction reactions occurring in the anaerobic breakdown of organic matter are as follows (Klein et al, 1972):

$$Carbon, C \rightarrow organic\,acids(R \bullet COOH) \rightarrow CH_4 + CO_2 \qquad \textbf{Equation 1}$$

$$Nitrogen, N \rightarrow amino\,acids[R \bullet (NH_2) \bullet COOH] \rightarrow NH_3 + amines \qquad \textbf{Equation 2}$$

$$Sulphur, S \rightarrow H_2S + organic\,S\,compounds \qquad \textbf{Equation 3}$$

$$Phosphorus, P \rightarrow PH_3 + organic\,P\,compounds \qquad \textbf{Equation 4}$$

Vinasse Characteristics

Composition Profile

Vinasse represents a mixture of water, organic and inorganic compounds (Cortez and Brossard Pérez, 1997). The mixture is dependent on the raw material used in the alcohol fermentation process. The temperature of the vinasse is in the range of 65º to 105° C (149-221°F). Vinasse has a light brown color with a solid content from 20,000 to 40,000 mg/l when obtained from straight sugarcane juice, and a black-reddish color with total solids ranging from 50,000 to 100,000 mg/l when obtained from sugarcane molasses. In addition, vinasse is an acidic liquid with pH between 4 and 5 and high chemical oxygen demand (COD) content (Tables 1 and 2). The inorganic solids contain considerable amounts of nutrients such as phosphorus, nitrogen and potassium (Table 1).

Environmental Limits

Many researchers (Cortez and Brossard Pérez, 1997; Barreto de Menezes, 1980; Paturau, 1969) have reported major environmental problems for the appropriate disposal of vinasse, which is understandable given the fact that BOD effluent discharge limits for most of environmental regulations throughout the world range from 30 to 100 mg/l for water and land disposal methods (Corbitt, 1989). Furthermore, the hydrogen sulfide, amines and other offensive-smelling chemicals that are generated by decomposition of the organic matter seem to add to vinasse's reputation as a difficult residual effluent. In Brazil, vinasse is disposed as irrigation water (Donzelli and de Souza, 2003). However, in other countries, vinasse treatment before disposal is required by federal and state environmental regulations due to its high BOD concentration (Appendix B, Tables B-1, B-2 and B-3).

Table 1. Comparative composition of vinasse derived from sugar cane

Component	Brazil (1) Juice	Brazil (2) Molasses	Australia (1) Molasses	Australia (2) Molasses	India Molasses	USA (La) Molasses
K, mg/l	1,733	4,893	8,767	10,704	4,078	9,073
P, mg/l	71	102	20	12	5,097	1
N, mg/l	102	408	3,160	1,835	1,019	153
Ca, mg/l	408	714	1,121	2,039	n.a.	143
Mg, mg/l	102	204	1,529	1,325	n.a.	61
Ash, mg/l	15,292	19,879	32,622	n.a.	n.a.	50,972
Organic Solids, mg/l	52,399	47,200	n.a.	n.a.	n.a.	n.a.
Total Solids, mg/l	68,201	n.a.	n.a.	91,750	69,322	n.a.
pH	4.6	4.8	n.a.	n.a.	4.3	4.5

Source: Cortez, L.A.B., and L.E. Brossard Perez. Experiences on vinasse disposal. Part III: Combustion of

vinasse-#6 fuel oil emulsions, Brazilian Journal of Chemical Engineering,Vol 14, No.1, 1997, São Paulo, Brazil.

Note: Data converted to mg/l from original % composition

n.a. means not available

Table 2. Vinasse composition used for modeling study

Component		
	Range	Range
pH	4-5	4-5
	mg/l	lb/cu ft
BOD	17,000 - 50,000	1.06 - 3.12
COD	20,000 - 60,000	1.25 - 3.75
Total solids	30,000 -70,000	1.87 - 4.37
Total nitrogen	300-800	0.01 - 0.05
Total phosphorus (as phosphates)	100-500	0.01 - 0.03
Total potassium (K_2O)	2,000 - 3,000	0.12 - 0.19
Ash	3,000 - 10,000	0.19 - 0.62

Adapted from Cortez, L.A.B., L.E. Brossard Perez, Experiences on Vinasse Disposal, Part III:

Combustion of vinasse-#6 oil emulsions, Brazilian Journal of Chemical Engineering, Vol. 14,

No. 1, 1997, São Paulo, Brazil.

Methodology

Anaerobic Digestion of Vinasse

Process Description
Operationally, biological waste treatment is typically accomplished using a digester such as that shown in Figure 1, which is proposed for the digestion of vinasse. The process apparatus consist of several basic components, including a feedstock (vinasse) storage and handling system, digester tank (reactor), gas and residue recovery systems, and if electricity is to be produced, a gas-burning engine/generator set.
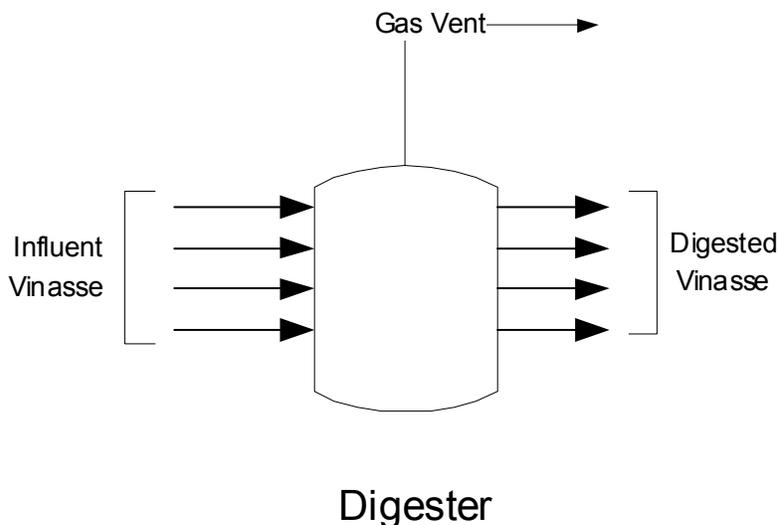
Digester

Figure 1. Schematic representation of digester used for anaerobic digestion.

The process starts as vinasse is introduced into the reactor where anaerobic bacterial culture is maintained in suspension. Temperature of influent vinasse was assumed as 40° C (104° F). The process is carried out in an airtight complete-mix reactor. Vinasse is retained in the reactor for an average period of time equivalent to 10 days, which is the literature-recommended residence time for anaerobic digestion at 40ºC in a complete mix reactor (Metcalf and Eddy, 1991). The bacterial culture carried out the conversion of the organic material to a variety of end products including methane (CH_4), carbon dioxide (CO_2), ammonia (NH_3) and cell or bacterial mass. As the methane gas is highly insoluble in water, the resulting gas mixture is collected in the dome of the reactor and withdrawn for energy recovery. The resulting cell tissue can be removed from the treated liquid by gravity settling because cell tissue has a specific gravity slightly greater than that of water (Metcalf and Eddy, Inc., 1991). The effluent or digested vinasse withdrawn from the reactor is reduced in organic load (BOD) by 90%. Digested vinasse is basically a mix of water and inorganic and organic compounds.

The bacteria chosen for the process were both, mesophilic and thermophilic. For the purpose of this study, (Table 2) BOD concentration in vinasse was assumed to be in the range of 1.06 to 3.12 lb/ft^3 (17,000 to 50,000 mg/l). The anaerobic digestion of organic matter is an oxidation-reduction reaction involving water and occurring within the pH range 6.5-8.0.

Mathematical Model (MADM)

A mathematical model using Microsoft Excel® (MADM) was developed with the purpose of evaluating the design parameters for this study. The MADM was configured in such a way that an output is provided for any size of ethanol producing facility input in the model data or for any change in the data fed to the model. In addition, the MADM has the capabilities of calculating the tonnage of cane required for the production of the ethanol, based on sucrose content in sugar cane and fabrication extraction parameters.

Calculations featured anaerobic digestion of vinasse for a distillery producing 10 million gallons/year of ethanol (37,850,000 l/yr), for which the calculated amount of vinasse was approximately 120,000,000 gallons/year. Vinasse production was equivalent to 800,000 gallons of vinasse per day (3,028,000 l/day) for 150 days of operation, 7 days per week and 24 hours per day.

Several equations were input into the mathematical model for the calculation of the anaerobic digestion process parameters, which are the following:

Volume of Methane

Equation 5 calculated the volume of methane

$$V_{CH_4} = (5.62)\left[(S_o - S)(Q)(8.34) - 1.42 P_x\right]$$ **Equation 5**

Where V_{CH4} =volume of methane produced at standard conditions (32° F and 1 atm), cu ft/day
    5.62 = theoretical conversion factor for the amount of methane produced from the complete conversion of one pound of BOD to methane and carbon dioxide, cu ft CH_4/lb BOD oxidized
    Q = flow rate, Mgal/day
    S_o = ultimate BOD in influent, mg/l
    S = ultimate BOD in effluent, mg/l

Mass of Cellular Tissue Production during Digestion

For a complete-mix, high rate digester without recycle, the mass of biological solids synthesized daily (P_x) was calculated using Equation 6 (Metcalf & Eddy, Inc., 1991).

$$P_x = \frac{Y\left[(S_o - S)(Q)(8.34)\right]}{1 + k_d \theta_c}$$ **Equation 6**

Where   Y= yield coefficient, lb/lb
        K_d = endogenous coefficient, day^{-1}
        θ_c = mean cell-resident time, day
        Other terms are as defined above.

The kinetic coefficient (endogenous coefficient) recommended in the literature for substrate similar in composition to vinasse (fatty acid) was 0.04 d^{-1} and the yield coefficient was 0.05 lb of cell/lb of BOD (Metcalf & Eddy, Inc. 1991).

Digester Volume

The volume of the digester was calculated (Appendix C) using Equation 7 (Levenspiel, 1972; Metcalf & Eddy, Inc., 1991).

$$V_r = Q(\theta_c)$$ **Equation 7**

Electrical Power

The volume of methane generated during the anaerobic digestion was used to calculate the electrical energy output. Methane gas at standard temperature and pressure has a net heating value of 960 Btu/cu ft. The low heating value of digester gas is roughly 600 Btu/cu ft, because digester gas is a mixture of approximately 60% methane and the rest being CO_2, hydrogen sulfide, particulates and water vapor (Metcalf and Eddy, 1991). By comparison, natural gas, which is a mixture of methane, propane and butane, has a low heating value of approximately 1000 Btu/cu ft.

The net electrical output was calculated using Equation 8 (Kirby, 2003).

$$\eta_{Overall} = \frac{\text{Net Electric Output}}{\text{Fuel Input}}$$ **Equation 8**

The overall thermal efficiency used for calculation purposes was 90%.

Performance Parameters

The MADM also evaluated several parameters of fundamental importance for anaerobic digestion. Among these parameters are the organic loading rate (volumetric loading rate), the volume of gas produced per pound of BOD in the influent and the food to microorganism (F/M) ratio.

The volumetric loading rate is expressed as the weight of organic or volatile feed sludge added per volume of digester per day, for example, lb BOD/cu ft day.

The volume of gas produced per pound of BOD in the influent is expressed as cu ft of gas/lb BOD destroyed in the vinasse influent, while the F/M ratio was expressed as lb BOD in the vinasse influent/lb of cellular tissue produced.

In addition, two gas productivity parameters were evaluated from the model's results. One of these parameters was the volume of methane gas produced per volume of ethanol produced, which was expressed as cu ft methane/cu ft of ethanol. The other parameter was the volume of methane gas produced per volume of vinasse processed, which was expressed as cu ft methane/cu ft of vinasse.

Basic Assumptions

1. It was assumed that the vinasse BOD concentration was reduced by 90% during anaerobic digestion. Due to vinasse strategic composition of organic acids, the digester efficiency of waste utilization should be much higher (90 to 97% of BOD content) than that of conventional organic sludge (60 to 70% of BOD content), since steps (1) and (2) of the three stage oxidation-reduction

anaerobic digestion are already completed before entering the reactor (Appendix A, Figure A-1). Several researchers (Marshall and Kopp, 2006 and Manohar Rao, 1999) have reported BOD reduction of 90% or more for the anaerobic digestion of vinasse.

2. It was assumed that anaerobic digestion of vinasse takes as little as 10 days, instead of the 30 to 40 days taken by conventional anaerobic digestion. Since vinasse is free of heavy metals and other toxic materials found in conventional wastewater sludge, better digestion process leading to shorter residence time can be expected.

3. It was assumed that the concentration of microorganisms in the influent was negligible.

Calculation Overview

The digester data and Equations 5 through 8 were input into the MADM and calculations were performed for constant volumes of vinasse in the digester feed while varying concentration of BOD in the vinasse. Influent vinasse BOD concentrations ranging from 1.06 to 3.12 lb/cu ft (17,000 to 50,000 mg/l) were used for the calculations (Table 2). In addition, vinasse was assumed to contain 1.87 to 4.37 lb/cu ft (30,000 to 70,000 mg/l) of total solids and moisture content ranging from 93 to 97%. Vinasse specific gravity was assumed to be in the range of 1.02 to 1.04.

Results and Discussion

Mathematical Model Output

The MADM output provided the calculated parameters for the anaerobic digestion of vinasse. The model results for the featured distillery are shown in Table 3 and Figures 2 through 4.

Calculated Parameters Data

Calculated data (Table 3) indicate that when vinasse BOD concentration ranged from 1.06 to 3.12 lb/cu ft (17,000 to 50,000 mg/l) the digester volume for vinasse anaerobic digestion decreased from 1,048,836 to 440,857 cu ft (29,697 to 12,482 kl). In addition, the digester volume decreased exponentially with BOD concentration increase (Figure 2), which is expected for the graphical representation of the design equation for a mixed reactor (Levenspiel, 1972).

Calculated data (Table 3) indicate that a high-rate reactor is required for anaerobic digestion of vinasse, since volumetric loading rates ranged from 0.11 to 0.76 lb/cu ft day (1.73 to 12.13 mg/l day). Literature data (The water Pollution Control Federation, 1976; Metcalf & Eddy, Inc., 1991) designate high-rate digesters as those having loading rates ranging from 0.10 to 0.40 lb/ft³ day when the hydraulic detention period ranged from 10 to 20 days, which is in agreement with the digester used for this study (hydraulic retention time of 10 days).

Table 3. Results of the MADM calculated parameters for anaerobic digestion of vinasse

|	Influent vinasse BOD, mg/l / lb/cu ft			
	17,000	**30,000**	**40,000**	**50,000**
Calculated Parameter	**1.06**	**1.87**	**2.50**	**3.12**
Influent vinasse BOD volumetric loading, lb/cu ft day	0.11	0.32	0.56	0.76
Influent vinasse BOD volumetric loading, mg/l day	1.73	5.15	8.97	12.13
Digester volume, cu ft	1,048,836	623,192	477,063	440,857
Digester volume, kl	29,697	17,645	13,507	12,482
Net mass of cell tissue (Px), lb/day	3,658	6,455	8,606	10,758
Volume of methane produced, cu ft/day	546,387	964,213	1,285,617	1,607,021
Volume of methane produced, l/day	15,470,283	27,300,499	36,400,665	45,500,831
Volume of gas produced, cu ft/day	910,645	1,607,021	2,142,695	2,678,369
Volume of gas produced, l/day	25,783,804	45,500,831	60,667,775	75,834,718
Effluent vinasse BOD , mg/l	1700	3000	4000	5000
Effluent vinasse BOD , lb/cu ft	0.11	0.19	0.25	0.31
Power generated, megawatts	3.60	6.36	8.48	10.60
Gas production/weight of volatile solids destroyed, cu ft/lb	8.92	8.92	8.92	8.92
Gas production/weight of volatile solids destroyed, l/mg	0.56	0.56	0.56	0.56
Food to microorganisms ratio, mg BOD/mg cell mass	31.03	31.03	31.03	31.03
Productivity rate, cu ft methane/cu ft ethanol, l/l	61.31	108.19	144.26	180.32
Productivity rate, cu ft methane/cu ft vinasse, l/l	5.11	9.02	12.02	15.03
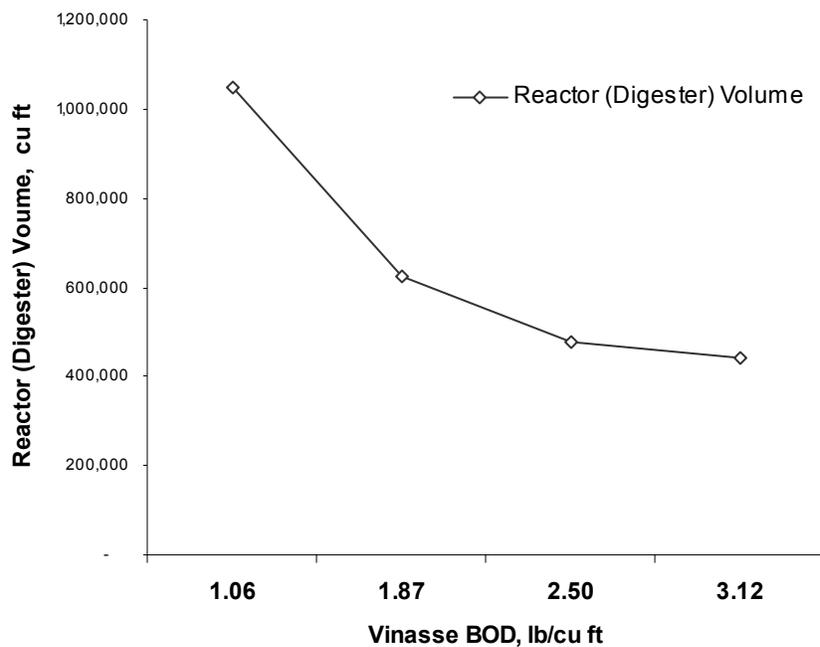
Figure 2. Reactor (digester) volume for anaerobic digestion

The calculated gas production per lb BOD destroyed was 8.92 cu ft/lb (Table 3), which is in agreement with values of 8.0 to 18.0 cu ft /lb found in the literature for typical anaerobic digestion of organic matter (The Water Pollution Control Federation, 1976, Metcalf & Eddy, Inc., 1991).

In addition, the calculated F/M ratio was 31.03 lb BOD/lb cell mass (Table 3). A high F/M ratio (20 to 30 lb BOD/lb cell mass) is beneficial for rapid removal of the soluble organic in the influent, since it provides high substrate driving force for quick absorption into the cellular mass (Metcalf & Eddy, Inc., 1991).

The volume of methane and total gas produced was nearly proportional to the rate of organic loading (Figure 3). The Water Pollution Control Federation (1976) reported similar results, which stated that the former is true for both the average 24-hour loading rate and the instantaneous loading rate.

The power generation capabilities as a result of anaerobic digestion ranged from 3.60 to 10.60 megawatts (Figure 4), which seem to indicate that the power generated could satisfy the power requirements of the entire distillery. This represents significant savings for the production of ethanol from sugarcane. The power output is also proportional to the organic loading rate, as expected (Figure 4).
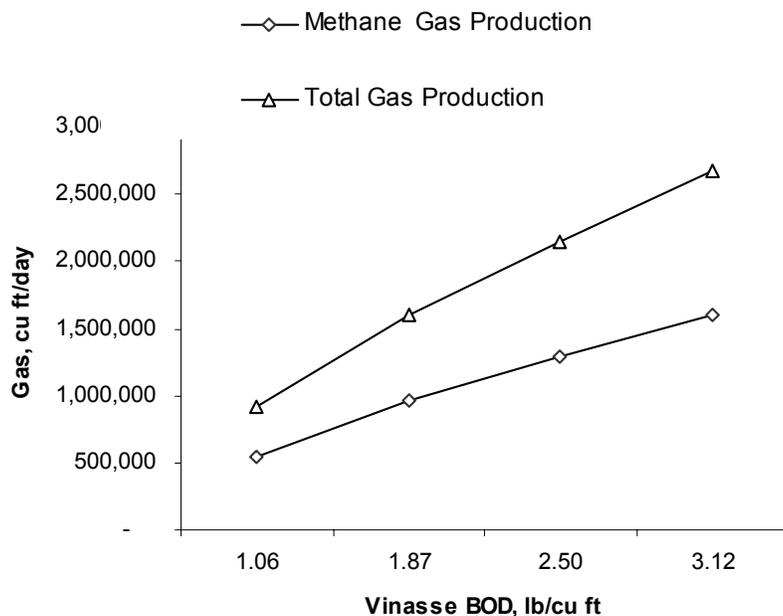

Figure 3. Gas production from anaerobic digestion of vinasse

There are several options for the gas produced, which provide great payback to the sugarcane distillery. If a gas turbine is installed, the methane can be used to produce "green" power for the distillery. In addition, the turbine exhaust gases can generate steam needed for the ethanol distillery. The biogas that is not converted into electricity can be scrubbed to pipeline specifications natural gas, compressed and injected into the existing natural gas distribution grid. Thus, the distribution lines are used as the storage system (Ethanol Producer Magazine, 2006).

The volume of methane gas produced per volume of ethanol produced ranged from 61.31 to 180.32 cu ft methane/cu ft ethanol when BOD in vinasse ranged from 1.06 to 3.12 lb BOD/cu ft vinasse (17,000 to 50,000 mg/l). The volume of methane gas produced per volume of vinasse processed ranged from 5.11 to 15.03 when BOD in vinasse ranged from 1.06 to 3.12 lb BOD/cu ft vinasse (17,000 to 50,000 mg/l).

Calculations by the MADM represent methane generated from BOD conversion only, however, it have been reported that 70 % or more of the COD is also converted to methane (Manohar Rao, 1999), therefore, the methane capabilities of the process are expected to be greater than the one shown (Figure 3), which further complements the process productivity. However, pretreatment by ozone before anaerobic digestion might be needed to destroy phenolic compounds present in vinasse, which could be toxic to the anaerobic bacteria (Santos M. et al, 2003).
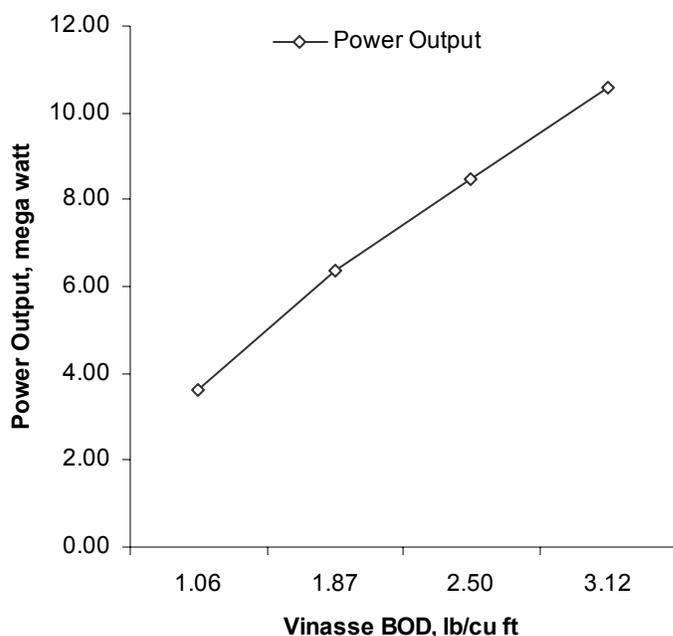

Figure 4. Power output using gas from anaerobic digestion

As the BOD content of the digester effluent vinasse is ranging from 0.11 to 0.31 lb/cu ft (1,700 to 5,000 mg/l), it is still over the range for allowed BOD effluent discharge for most environmental regulations throughout the world (30 to 100 mg/l). The residual effluent vinasse must be further processed to reduce the BOD and COD content for appropriate disposal (Table 3). However, this hurdle presents further opportunities for energy recovery. Concentration of the digested vinasse, either by evaporation or ultrafiltration could produce additional energy for the distillery. If the digested vinasse is evaporated to 65% solids, energy could be recuperated by burning the digested vinasse. If the vinasse is ultra-filtrated, potable water could be produced from the filtrate stream, while the concentrated stream could be burned for energy recovery or sold as a liquid fertilizer. The ash left after burning could be used as a fertilizer as well. Due to its high mineral content, vinasse creates optimum environmental conditions for the microorganisms involved in the digestion process, thus resulting in savings on process nutrient requirements and process economics.

Since the generation of biogas constitutes a non-conventional energy source, extra benefits could be obtained through the utilization of incentives and funding currently available from government legislation aimed at facilitating non-petroleum derived energy production. In addition to the clean ecological benefit, this process promotes energy savings and recovery.

Furthermore, extra energy savings in the distillery could be obtained by using vinasse to heat process water. Vinasse that comes out of the distillation process is in the range of 65º to 105º C (149º to 221º F) and it needs to be cooled to about 40º C (104º F). Therefore a heat exchanger can be used to lower the temperature of the hot vinasse with cool process water. At the same time, the vinasse warms the process water for use in the distillery.

As the sugar distillery process constitute an intense user of surface water, the production of potable water from the digested vinasse sludge could further decrease production costs in the distillery, in addition to the potential of achieving zero waste generation and discharge. The creation of all these value-added products will certainly boost the reduction in production cost of the sugar-to-ethanol distillery.

Conclusions

The gas as well as the electrical energy produced by anaerobic digestion of vinasse is proportional to the concentration of BOD in the vinasse influent. The volume of the digester decrease exponentially when BOD concentration in the influent vinasse increases. Therefore, optimal reactor size is obtained when BOD concentration in the influent vinasse is the highest. The implementation of the anaerobic digestion of vinasse will improve distillery productivity, as green energy is produced at the same time that other byproducts could also be produced.

The (MADM) is an effective tool for predicting the process of anaerobic digestion of vinasse, as calculated parameters correlated with available experimental data. Bio-methane production from the sugar distillery is an excellent process improvement project, as it has the potential to meet the fuel and steam requirements of the distillery, in addition to the potential environmental benefits. Greenhouse gas emissions could be reduced from replacing existing fossil fuel sources. In

addition, the production of "green" electrical power could earn further economic benefits by qualifying the distillery for available government-sponsored credits and other incentives.

Anaerobic digestion of vinasse constitute a good strategy for improving the disposal conditions of vinasse, since it reduces the BOD content, while gas of high calorific value is produced. With the ever-escalating energy prices, the methane produced could represent reduction of production costs of the distillery.

The implementation of such an intensive energy recovery, water recycling and value-added byproducts process such as the one encompassed by anaerobic digestion of vinasse, is certainly bound to create a huge improvement in the public relations image of the sugar industry. In addition to obtaining economical credits by the creation of value-added product and green energy production, anaerobic digestion could certainly tip the balance positively into an economic feasible sugar-to-ethanol distillery.

Recommendations

Due to the relevance of vinasse on the sugar cane distillery, the following alternatives are worth pursuing:

- Evaluation of the economics and viability of the anaerobic digestion of vinasse by conducting a feasibility study, as the process provides an alternative to high-priced natural gas.

- Evaluation of the production of potable water and fertilizer from the digested vinasse, which can potentially create greater value-added products for the ethanol distillery. Mineral-rich vinasse is an excellent substrate for fertilizer production.

- Evaluation of the use of the cell tissue mass discarded from the anaerobic digestion process for use as an additive to fertilizer.

Acknowledgements

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APPENDIX A

Process Biochemistry

The various chemical reactions brought about by bacteria are due to the activity of enzymes or "ferments" elaborated by the bacterial cells. Test of different bacteria indicate that they are about 80% water and 20% dry material, of which 90% is organic and 10% inorganic. An approximate formula for the organic fraction is $C_5H_7O_2N$ (Metcalf and Eddy, Inc., 1991).
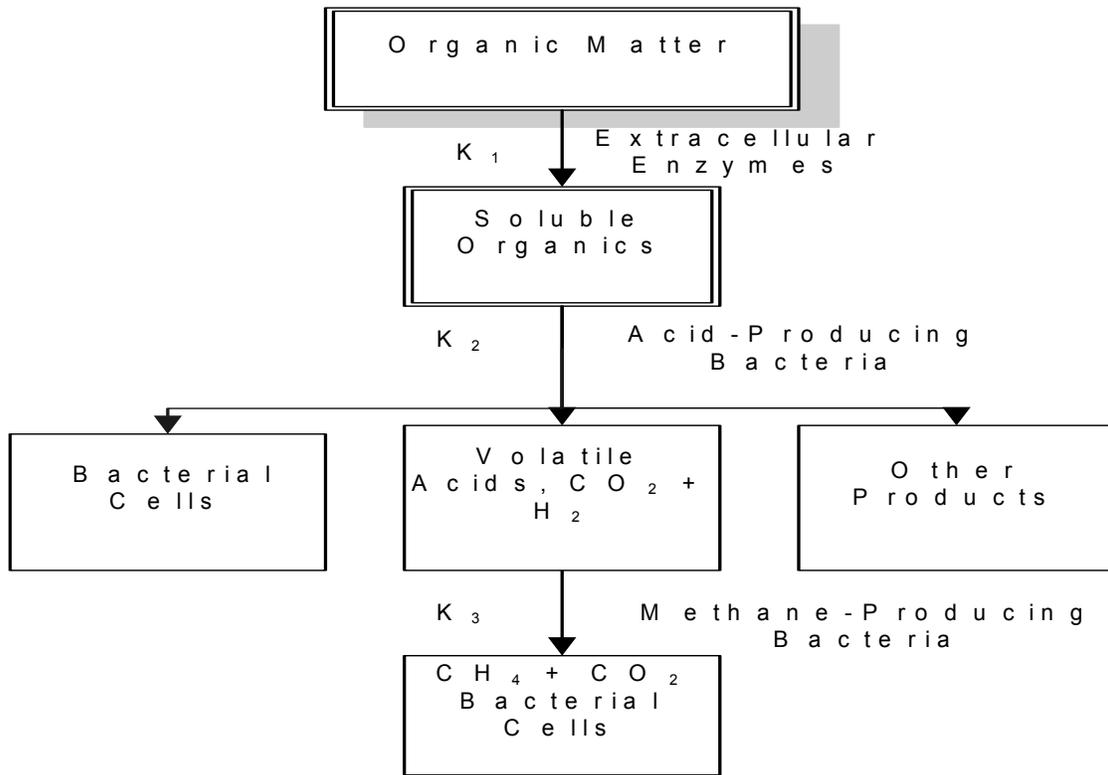
To continue to reproduce and function properly, an organism must have (1) a source of energy, (2) carbon for the synthesis of new cellular material, and (3) inorganic elements (nutrients) such as nitrogen, phosphorus, sulfur, potassium, calcium and magnesium. Organic nutrients (growth factors) may also be required for cell synthesis. Two of the most common sources of cell carbon for microorganisms are organic matter and carbon dioxide. The energy needed for cell synthesis may be supplied by light or by a chemical oxidation reaction.

Required organic nutrients, known as "growth factors," are compound needed by an organism as precursors or constituents of organic cell material that cannot by synthesized from other carbon sources. Among the major growth factors are amino acids, purines and pyrimidines, and vitamins (Metcalf and Eddy, Inc., 1991).

The anaerobic decomposition of organic matter is a three-stage reaction: (1) hydrolysis of the organic material into soluble organic compounds, (2) acetogenesis, or conversion of soluble organics to volatile fatty acids (mostly acetic acid); and (3) methanogenesis, or conversion of the volatile fatty acids into methane (Klein et al, 1972, Metcalf & Eddy, Inc., 1991).

The types of microorganisms involved in acetogenesis are often identified as "acidogens" or "acid formers" and among these are clostridium spp., peptococcus anaerobus, Bifidobacterium spp., Desulphovibrio spp., Corynebacterium spp., Lactobasillus, Actinomyces, Staphylococcus, and Escherichia coli. Other physiological groups include those producing proteolytic, lipolytic, ureolytic or cellulytic enzymes.
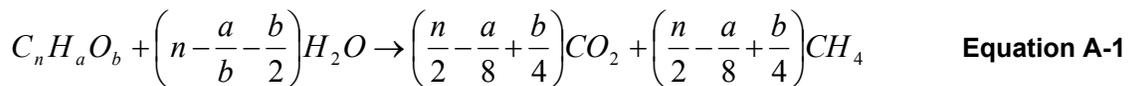
The bacteria responsible for methanogenesis are identified as "methanogens," or "methane formers (Metcalf & Eddy, Inc., 1991)." The principal genera of microorganisms that have been identified include the rods (Methnobacterium, Methanobacillus) and spheres (Methanococcus, Methanosarcina).
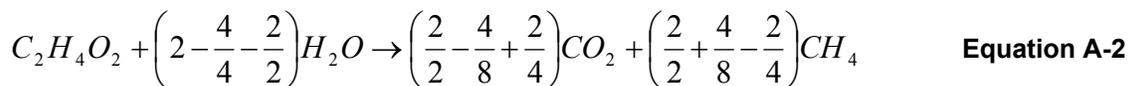
```
┌──────────────────────────────┐
│     Organic Matter           │
└──────────────────────────────┘
                  │  Extracellular
        K₁        │  Enzymes
                  ▼
        ┌──────────────────┐
        │    Soluble       │
        │    Organics      │
        └──────────────────┘
                  │  Acid-Producing
        K₂        │  Bacteria
    ┌─────────────┼─────────────┐
    ▼             ▼             ▼
┌─────────┐ ┌──────────┐ ┌──────────┐
│Bacterial│ │ Volatile │ │  Other   │
│ Cells   │ │Acids, CO₂+│ │ Products │
│         │ │   H₂     │ │          │
└─────────┘ └──────────┘ └──────────┘
                  │  Methane-Producing
        K₃        │  Bacteria
                  ▼
        ┌──────────────────┐
        │  CH₄ + CO₂       │
        │  Bacterial       │
        │  Cells           │
        └──────────────────┘
```

Anaerobic digestion of organic wastes. K_1, K_2 and K_3 refer to the rates of reaction.

Figure A-1. Stages of anaerobic digestion

In the digester the bacterial culture carries out the conversion in general accordance with elemental stoichiometric (Equation A-1).
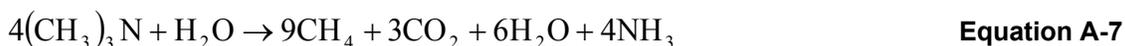
$$C_nH_aO_b + \left(n - \frac{a}{b} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CH_4 \qquad \textbf{Equation A-1}$$

In the case of anaerobic digestion of acetic acid, Equation A-2 can represent the reaction:

$$C_2H_4O_2 + \left(2 - \frac{4}{4} - \frac{2}{2}\right)H_2O \rightarrow \left(\frac{2}{2} - \frac{4}{8} + \frac{2}{4}\right)CO_2 + \left(\frac{2}{2} + \frac{4}{8} - \frac{2}{4}\right)CH_4 \qquad \textbf{Equation A-2}$$

It is important to note that methane bacteria can only use a limited number of substrates for the formation of methane. Currently, it is known that methanogens use the following substrates: $CO_2 + H_2$, formate, acetate, methanol, methylamines, and carbon dioxide.

Typical energy-yielding conversion reactions involving these compounds are as follows:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$ **Equation A-3**

$$4HCOOH \rightarrow CH_4 + 3CO_2 + 2H_2O$$ **Equation A-4**

$$CH_3COOH \rightarrow CH_4 + CO_2$$ **Equation A-5**

$$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$$ **Equation A-6**

$$4(CH_3)_3N + H_2O \rightarrow 9CH_4 + 3CO_2 + 6H_2O + 4NH_3$$ **Equation A-7**

In an anaerobic digester, the two principal pathways involved in the formation of methane are (1) the conversion of hydrogen and carbon dioxide to methane and water and (2) the conversion of acetic acid to methane and carbon dioxide (Equations A-3 and A-5, respectively).

Most biological treatment processes are comprised of complex, interrelated, mixed biological populations, with each particular microorganism in the system having its own growth rate (Metcalf and Eddy, Inc., 1991).

Nutrient Requirements

If a biological system is to function properly, nutrients must be available in adequate amounts. The principal nutrients are nitrogen and phosphorus. Based on an average composition of cell tissue of $C_5H_7NO_2$, about 12.4 % by weight of nitrogen will be required. The phosphorus requirement is assumed to be about one-fifth of this value. However, these are just typical values, as the percentage distribution of nitrogen and phosphorus in cell tissue varies with the age of the cell and environmental conditions.

Other nutrients required, but only in trace quantities, are sodium, potassium, calcium, chloride, sulfate and bicarbonate (Metcalf & Eddy, Inc., 1991).

Vinasse typically contains adequate amounts of nutrients (both inorganic and organic) to support biological treatment for the removal of carbonaceous BOD. In Brazil, most of the vinasse that results from ethanol production is being used as fertilizer due to high potassium content (Donzelli, Penatti and de Souza, 2003).

APPENDIX B

Vinasse Composition

Table B-1. Dry basis vinasse composition (molasses derived vinasse)

Component	As Received	Dry Basis
	%	%
Solids	29.79	n.a
Ash	13.31	18.95
Sulphur	0.08	0.12
Volatile matter	48.67	69.31
Fixed carbon	8.24	11.73
Carbon	n.a	39.72
Hydrogen	n.a	8.6
Nitrogen	n.a	1.65

Source: Cortez, L.A.B., L.E. Brossard Perez, Experiences on Vinasse disposal, Part III:

Combustion of Vinasse -#6 Fuel Oil, Brazilian Journal of Chemical Engineering, Vol. 14, No. 1,

1997, São Paulo, Brazil.

n.a. means not available

Table B-2. Analysis of vinasse from various raw materials used for ethanol fermentation

Components	Raw Material		
	Molasses	**Cassava**	**Sorghum**
pH	4.4	3.5	4.5
	mg/l	mg/l	mg/l
BOD	25,800	31,400	46,000
COD	48,000	81,100	79,900
Total Solids	68,000	44,500	34,100
Soluble Solids	57,100	40,400	n.a.
Fixed Solids	48,400	4,100	n.a.
Suspended solids	38,700	n.a.	n.a.
Organic matter	19,500	37,100	n.a.
Carbohydrates	8,000	20,100	3,400
Total Nitrogen	820	650	800
Total phosphorus (as phosphates)	480	380	100
Ash	10,700	10,500	6,100

Source: Barreto de Menezes, T. J., Etanol, o Combustible do Brasil (Ethanol, Brazil's fuel, in Portuguese language),

 1980, Editora Agronomica Ceres, Ltda, São Paulo, Brazil.

n.a. means not available

Table B-3. Dry basis vinasse composition (sugar cane juice vinasse)

Compound Name	Compound Amount
	%
Mineral matter	29
Sugar (reducing)	11
Proteins	9
Volatile acids	1.5
Gums	21
Combined lactic acid	4.5
Other combined organic acids	1.5
Glycerol	5.5
Wax, phenolic bodies, lignin, etc.	17

Source: Paturau, J.M., By-Products of the Cane Sugar Industry, an
Introduction to their Industrial Utilization, 1969, Page 183, Elsevier
Publishing Company, New York.

APPENDIX C

Process Design

Various methods are currently used for digester design and these are based on (1) the concept of mean residence time, (2) the use of volumetric loading factors, (3) observed volume reduction, and (4) loading factors based on population. For the purpose of this investigation, the concept of mean residence time will be considered. In addition, the anaerobic treatment process will be carried out in a complete-mix reactor without recycle.

A mass balance for the mass of microorganisms in the complete-mix reactor can be written as follows:

$$\begin{pmatrix} Rate\ of\ accumulation \\ of\ microorganisms \\ within\ the\ system \\ boundary \end{pmatrix} = \begin{pmatrix} Rate\ of\ flow\ of \\ microorganims \\ into\ the\ system \\ boundary \end{pmatrix} - \begin{pmatrix} Rate\ of\ flow\ of \\ microorganisms \\ out\ of\ the\ system \\ boundary \end{pmatrix} + \begin{pmatrix} Net\ growth\ of \\ microorganisms \\ within\ the\ system \\ boundary \end{pmatrix}$$

Simplified word statement:

Accumulation = Inflow – Outlfow + Net Growth   **Equation C-1**

Symbolic kinetic representation:

$$\frac{dX}{dt} V_r = QX_o - QX + V_r r_g'$$ **Equation C-2**

Where dX/dt = rate of change of microorganism concentration in the reactor measured
              in terms of mass (volatile suspended solids), mass
              VSS/unit volume. time
              V_r = reactor volume
              Q = flowrate, volume/time
              X_o = concentration of microorganism in influent, mass VSS/unit volume
              X = concentration of microorganisms in the reactor, mass VSS/unit
              volume

And that after reaching steady state conditions in the reactor $dX/dt = 0$
              r_g' = net rate of microorganism growth, mass VSS/unit volume. time

Where μ_m = maximum specific growth rate, time^{-1}

The solution of the design equation is accomplished after combining the above
mathematical expressions with the kinetic expression of biological growth in the bacterial
culture within the reactor, which takes into account the rate of growth of bacterial cells
and the rate of endogenous decay.

$$\frac{Q}{V_r} = \frac{1}{\theta} = \frac{\mu_m S}{K_s + S} - k_d$$ **Equation C-3**