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

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Objectives

- Data gathering and design parameters evaluation for subsequent feasibility study anaerobic digestion of vinasse
- Design parameters include:
  - Digester size
  - Volumetric loading rate
  - Volume of gas produced
  - Electric power generating capabilities
- Process improvement project for the distillery, as gas of high calorific value is produced as well as a stabilized sludge

Background

- Energy supply crunches and price spikes have focused attention on alternative energy sources
- Ethanol emerging as a transportation fuel
- Need for diversification of product portfolio
- Need for more efficient process & productivity
- Sugar-to-ethanol process presents opportunities for profitable use and disposal of vinasse

Background

- Production of 12 gallons of vinasse per gallon of ethanol
- Putting vinasse in a per capita basis, it is equivalent to 0.24 people per gallon of vinasse (for wastewater production of 50 gallons/person)
- A 110,000 gal/day ethanol distillery produces a volume of vinasse equivalent to the wastewater of a city with population of 768,000 people

Background

- Problems with adequate disposal, as environmental regulations for effluent discharge throughout the world range between 30-100 mg/l of biochemical oxygen demand (BOD)
- Hydrogen sulfide, amines and other offensive-smelling chemicals generated by decomposition of the organic matter, contribute to vinasse reputation as an unfriendly effluent

Vinasse-Dependence on Raw Material and Ethanol Process

- When obtained straight from sugar cane juice
  - Light brown color with 20,000 – 40,000 mg/l solid content
- When obtained from sugar cane molasses:
  - Black-reddish color with 50,000 – 100,000 mg/l solid content
- pH between 4 and 5
- BOD content between 10,000 and 50,000 mg/l

Comparative Geographic Vinasse Composition

	Brazil (1)	Brazil (2)	Australia (1)	Australia (2)	India	USA (La)
Component	Juice	Molasse	Molasse	Molasse	Molasse	Molasse
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

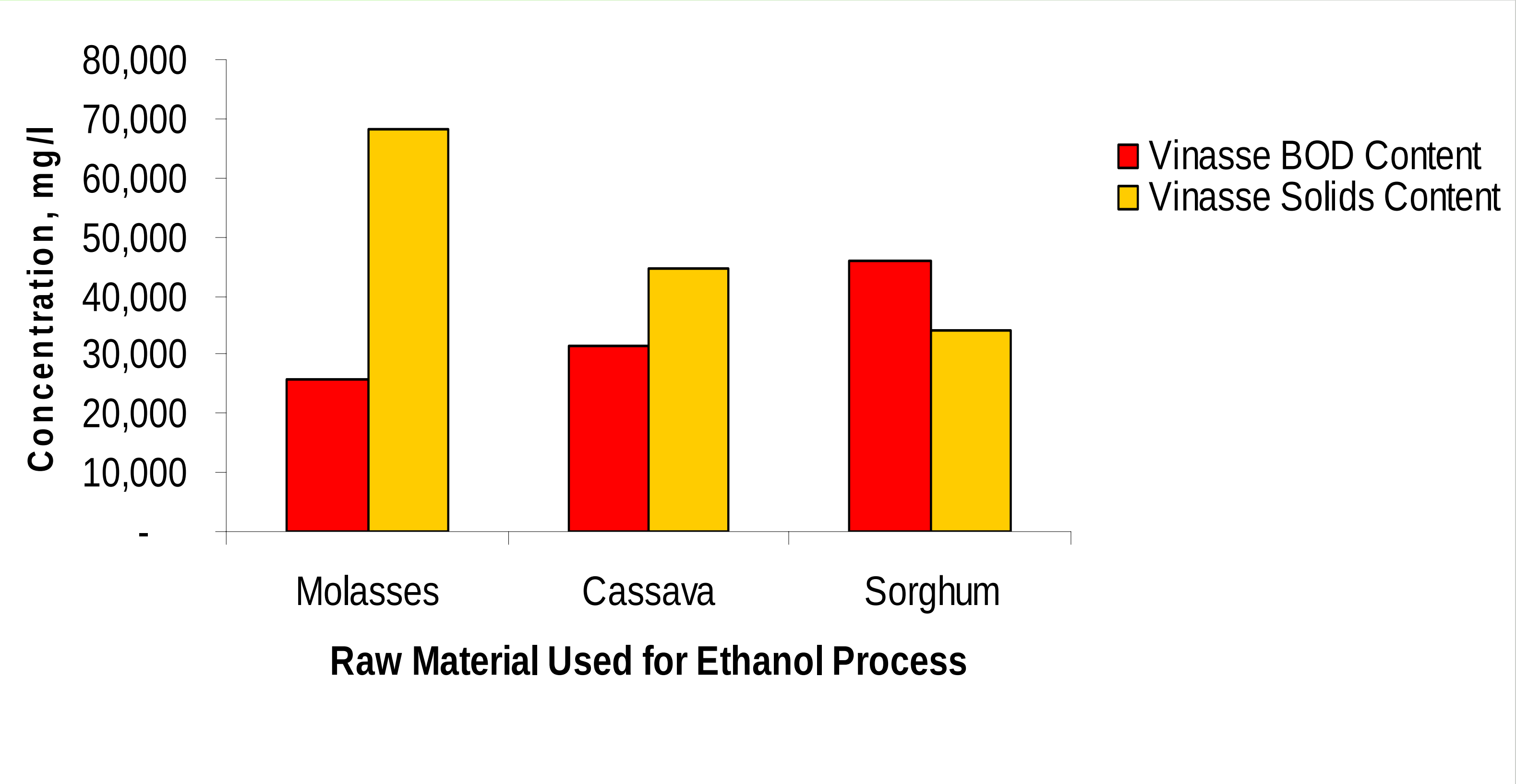
Comparative Vinasse Composition

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, Sao Paulo, Brasil

n.a. means not available

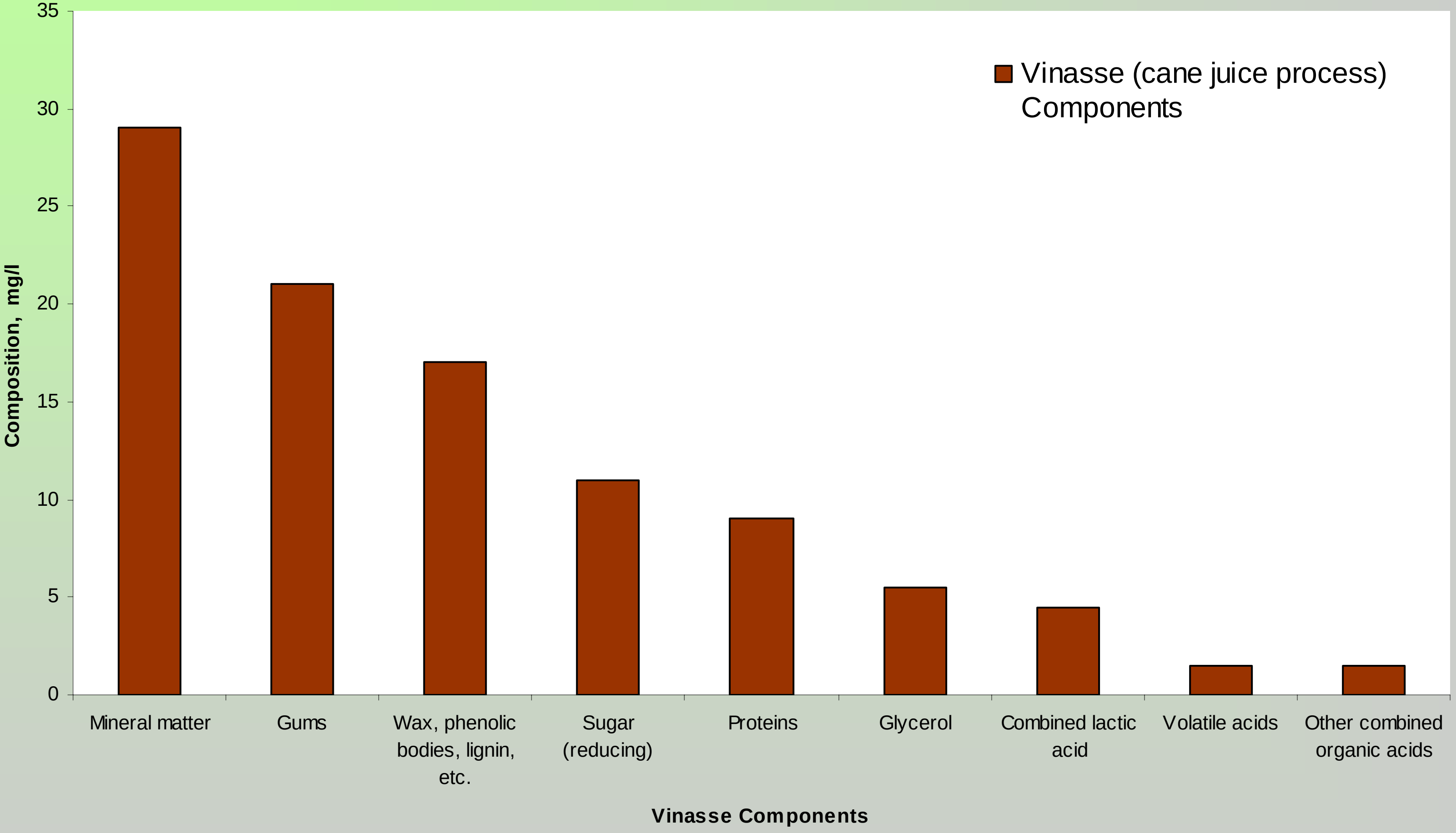
Comparative Vinasse Composition



Vinasse from Cane Juice Process

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.	

Vinasse from Cane Juice Process



Vinasse from Molasses Process

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. Sao Paulo, Brazil		
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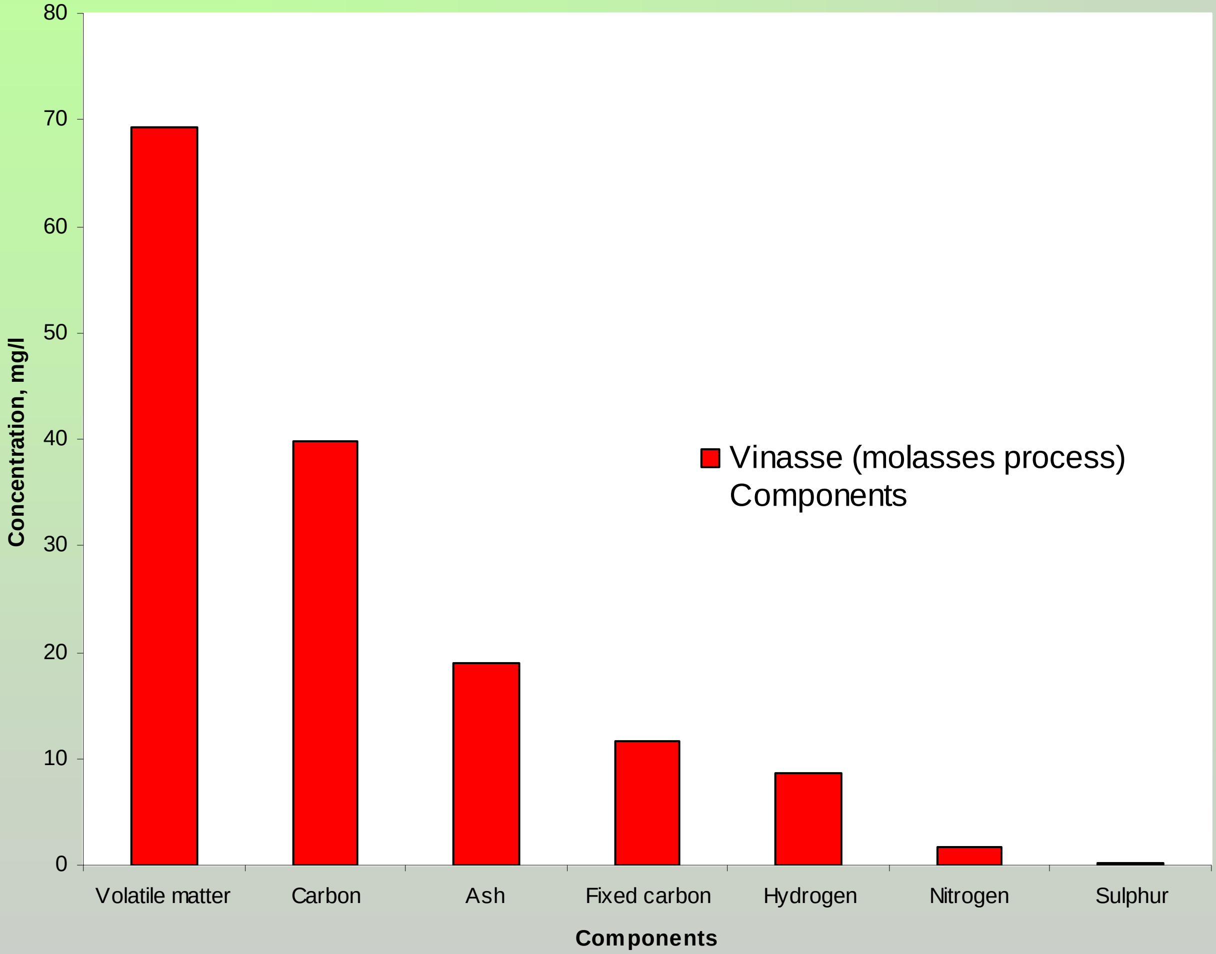
Vinasse from Molasses Process



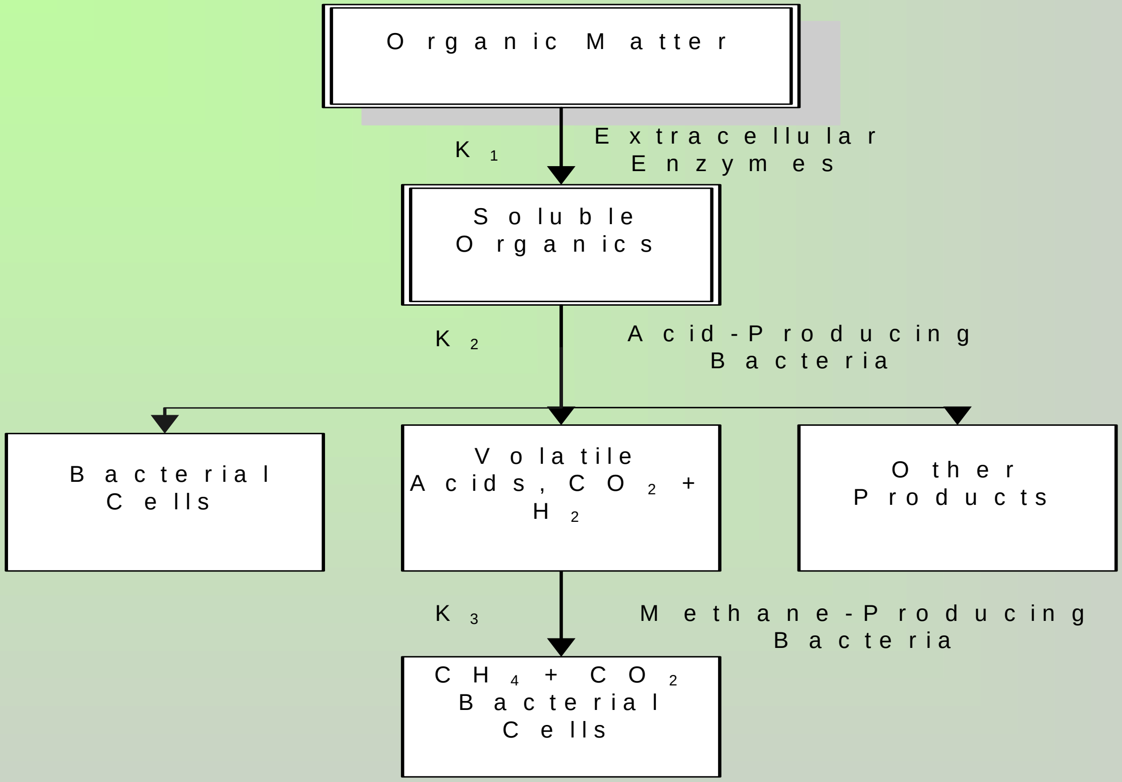
Biochemical Overview

- Anaerobic treatment is defined biochemically as the microbial conversion of organic compounds into carbon dioxide, methane and microorganism cells in the absence of free molecular oxygen (Corbitt, 1989)
- For organic nitrogen compounds, the end products will also include ammonia
- The various chemical reactions brought about by bacteria are due to the activity of enzymes or “ferments” elaborated by the bacterial cell.

Biochemical Overview

- 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)
- Anaerobic digestion is a oxidation reduction reaction consisting of three-stages named Hydrolysis, acetogenesis and methanogenesis

Anaerobic Digestion of Organic Matter



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

Process Description

In the digester, the bacterial culture carries out the conversion of organic matter in general accordance with the stoichiometric equation below (Klein, 1972):

$$C_nH_aO_b + \left(n - \frac{a}{b} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CH_4 \qquad \text{Eq. 1}$$

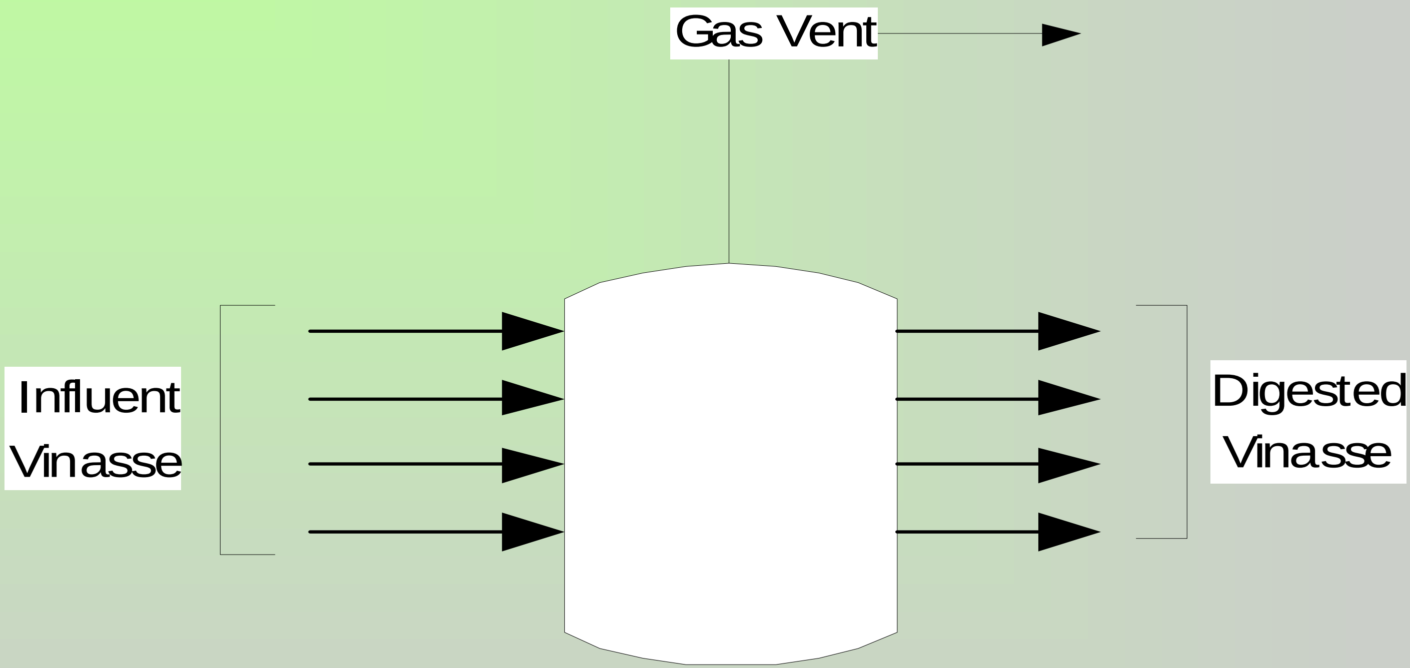
In the case of anaerobic digestion of acetic acid, the reaction can be represented by eq. 2

$$C_2H_4O_2 + \left(2 - \frac{4}{4} - \frac{2}{2}\right)H_2O \rightarrow \left(\frac{2}{2} - \frac{4}{8} + \frac{2}{4}\right)CO_2 + \left(\frac{2}{2} + \frac{4}{8} - \frac{2}{4}\right)CH_4 \qquad \text{Eq. 2}$$

Process Design – Reactor Size

- A complete-mix reactor without recycle was used for the model
- The method of mean residence time was selected

Process Design – Reactor (Digester)



Digester

Process Design – Reactor Size (Cont.)

- A mass balance on the microorganisms in the digester is given by equations 3-4:

$$\text{Accumulation} = \text{Inflow} - \text{Outflow} + \text{Net Growth} \qquad \text{Eq. 3}$$

$$\frac{dX}{dt} V_r = QX_0 - QX + V_r r'_g \qquad \text{Eq. 4}$$

Process Design – Reactor Size (Cont.)

- After reaching steady state conditions in the digester, dX/dt =0 and solution to equation 4 provides Eqs 5-7 (Metcalf & Eddy, Inc., 1991):

$$V_{CH_4} = (5.62)\left[(S_o - S)(Q)(8.34) - 1.42P_x\right] \qquad \text{Eq. 5}$$

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

Process Design – Reactor Size (Cont.)

- Where V_{CH4} =volume of methane produced at standard conditions (32º F and 1 atm), ft^3/day
- 5.62 = theoretical conversion factor for the amount of methane produced from the complete conversion of one pound of BOD_L to methane and carbon dioxide, ft^3 CH_4/lb BOD_L oxidized
- Q = Vinasse flow rate, Mgal/day
- S_o = Ultimate BOD_L in influent, mg/l
- S = Ultimate BOD_L in effluent, mg/l

Process Design – Reactor Size (Cont.)

$$V_r = Q(\theta_c) \qquad \text{Eq. 7}$$

- The electrical power is given by eq. 8 (Kirby, 2003)

$$\eta_{Overall} = \frac{\text{Net Electric Energy Output}}{\text{Fuel Heat Input}} \qquad \text{Eq. 8}$$

Basic Assumptions

- Operation temperature of anaerobic digestion: 40ºC (104°F)
- Efficiency of waste utilization during anaerobic digestion (E): 90%
- Overall thermal efficiency: 90%
- Methane heating value: 600 Btu/cu ft
- Vinasse specific gravity: 1.02 to 1.04

Distillery Production & Operation

Distillery Production Data	
Ethanol production, gal/year	10,000,000
Ethanol production, l/year	37,850,000
Vinasse production, gal/gal ethanol, l/l	12
Operation:	
Days/year	150
Hours/day	24
Days/week	7

Vinasse Composition Used for Study

Component		
	Range	Range
pH	4-5	4-5
	mg/l	lb/cu ft
BOD	17000-50000	1.06 - 3.12
COD	20000-60000	1.25 - 3.75
Total solids	30000-70000	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)	2000-3000	0.12 - 0.19
Ash	3000-10000	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, Sao Paulo, Brazil.

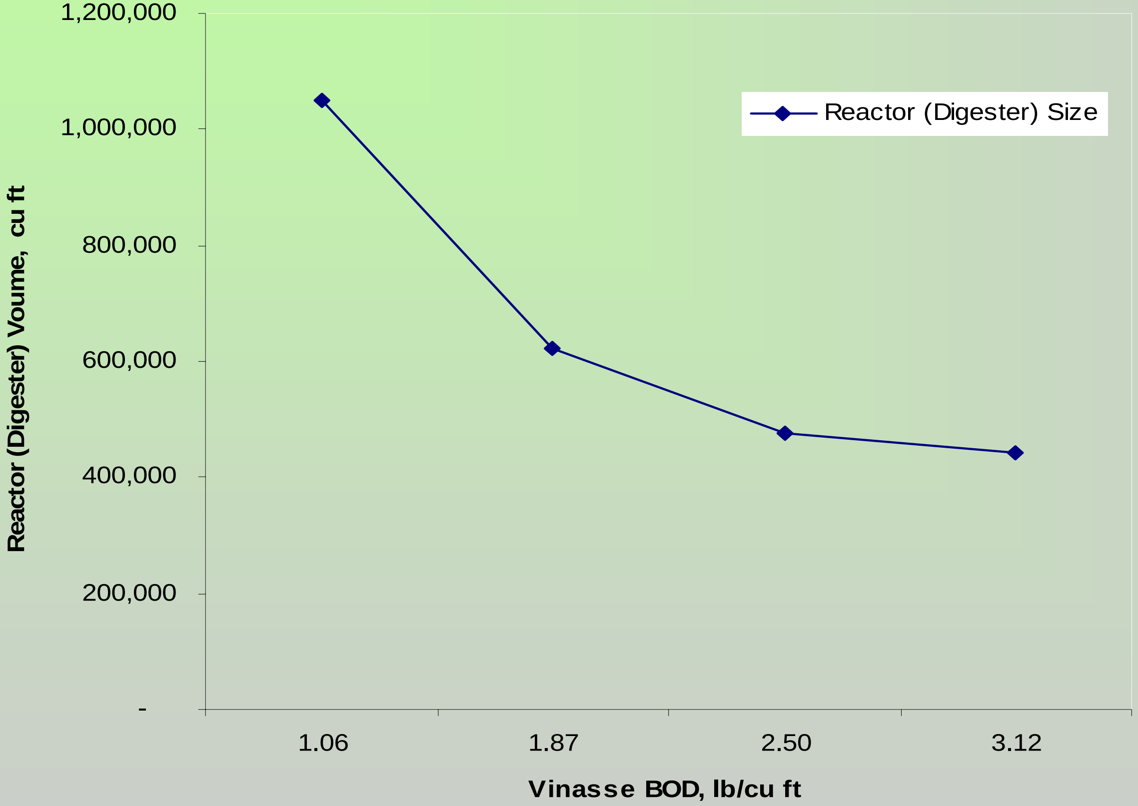
Model Results

	Calculated design parameters for anaerobic digestion of vinasse.			
Digester volume, cu ft	1,048,836	623,192	477,063	440,857
Digester Volume, gal	7,845,840	4,661,800	3,568,676	3,297,839
Influent vinasse BOD, mg/l	17000	30000	40000	50000
Influent vinasse BOD, lb/cu ft	1.06	1.87	2.50	3.12
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
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
Power generated, megawatts	3.60	6.36	8.48	10.60
Food to microorganisms ratio, lb BOD/Lb cell mass	31.03	31.03	31.03	31.03
Food to Microorganisms ratio, mg BOD/mg cell mass	31.03	31.03	31.03	31.03
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

Digester Volume

Influent vinasse BOD, mg/l	Digester volume, l	Effluent vinasse BOD , mg/l
17,000	29,696,503	1,700
30,000	17,644,912	3,000
40,000	13,507,439	4,000
50,000	12,482,321	5,000

Digester Volume



Volume of Methane Production

	Volume of methane produced, l/day	Volume of methane produced, cu ft/day
Influent vinasse BOD, mg/l		
17,000	15,470,283	546,387
30,000	27,300,499	964,213
40,000	36,400,665	1,285,617
50,000	45,500,831	1,607,021

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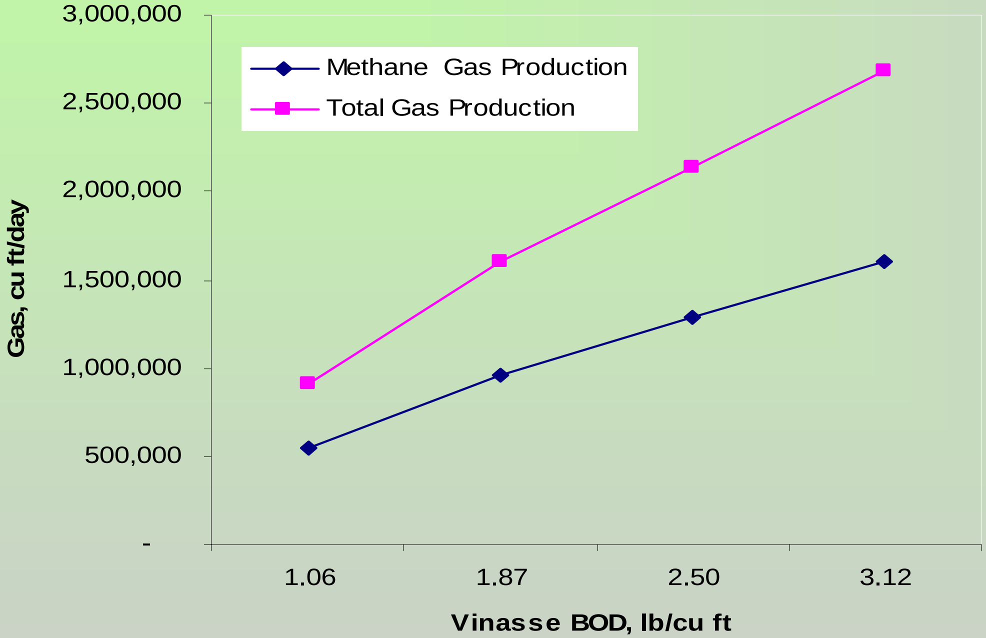


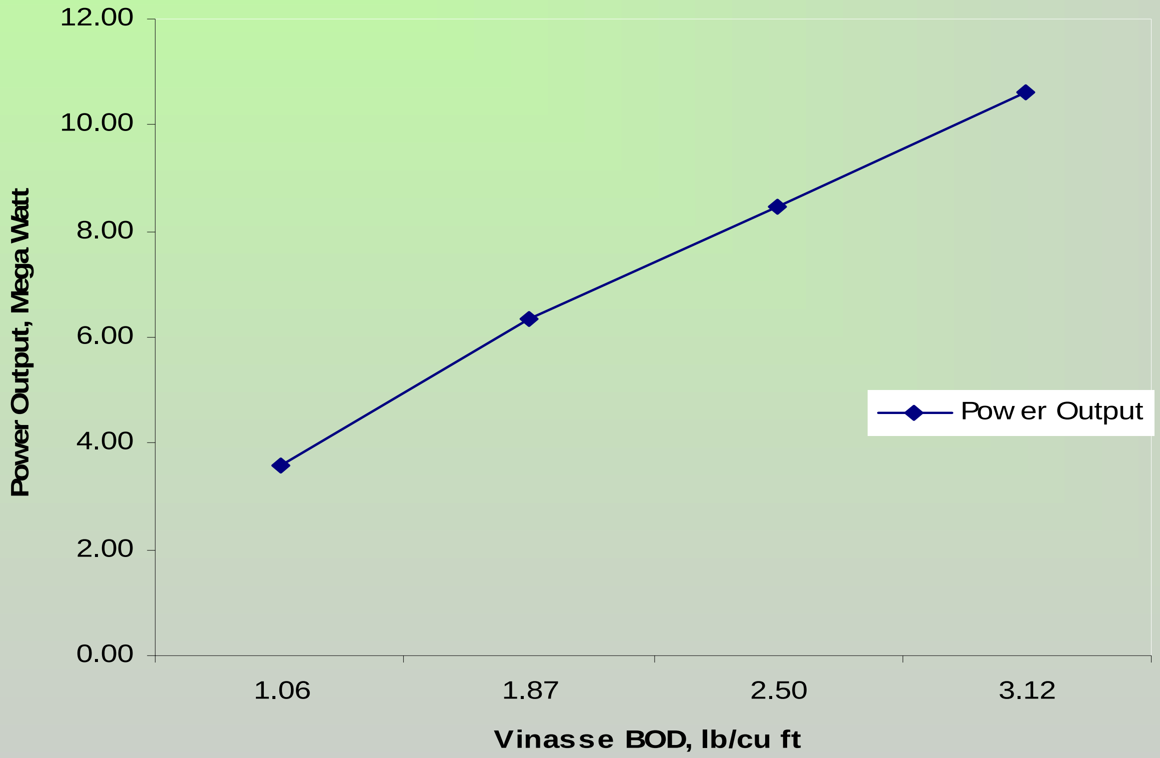
Results Discussion (Cont.)

- The volume of gas produced is nearly proportional to the rate of organic loading (BOD) in the influent, which is true for both the average 24-hour loading rate and the instantaneous loading rate (The Water Control Pollution Federation, 1976)

Power Generation

	Power generated, megawatts
Influent vinasse BOD, mg/l	
17,000	3.60
30,000	6.36
40,000	8.48
50,000	10.60

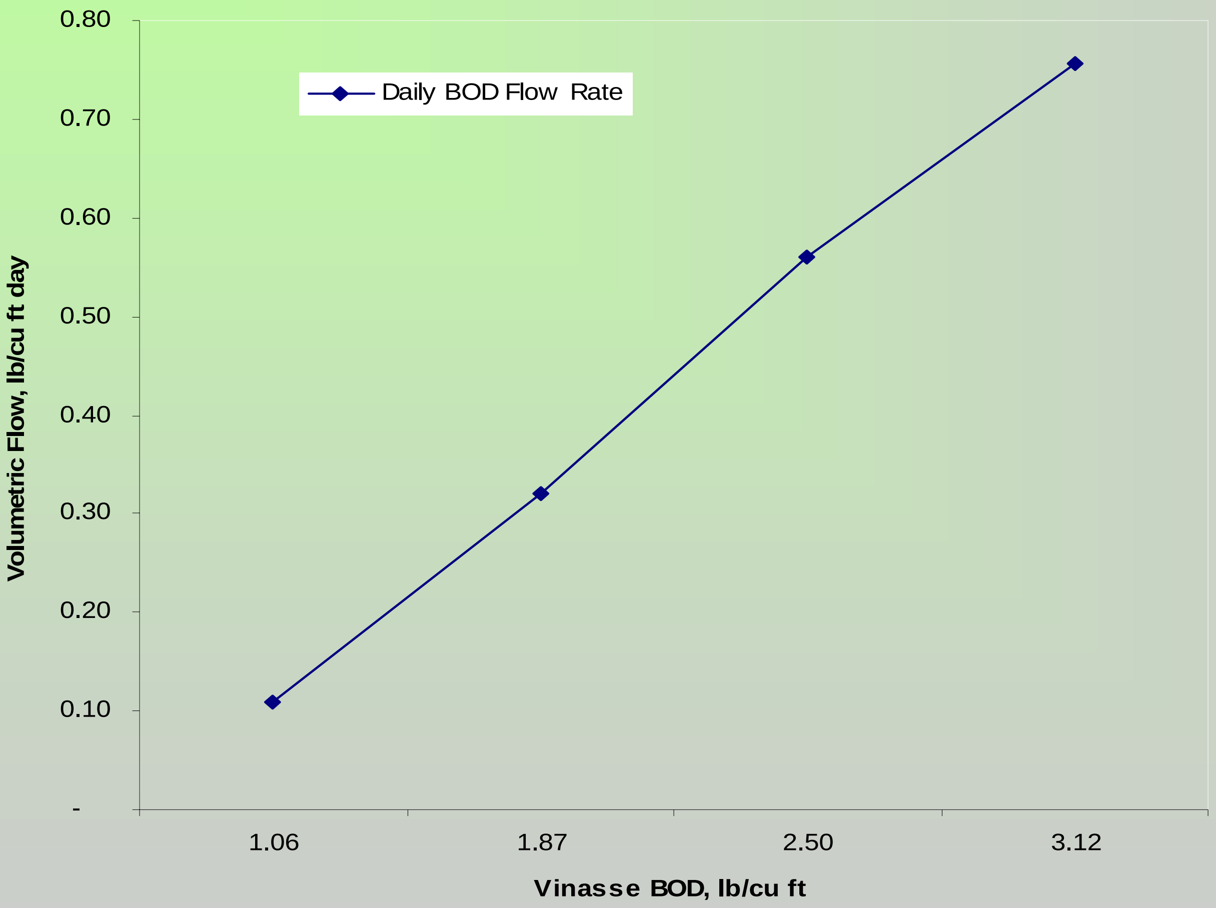
Power Generation



Volumetric Flow to Digester

	Influent vinasse BOD volumetric loading, mg/l day	Influent vinasse BOD volumetric loading, lb/cu ft day
Influent vinasse BOD, mg/l		
17,000	1.73	0.11
30,000	5.15	0.32
40,000	8.97	0.56
50,000	12.13	0.76

Volumetric Flow to the Digester



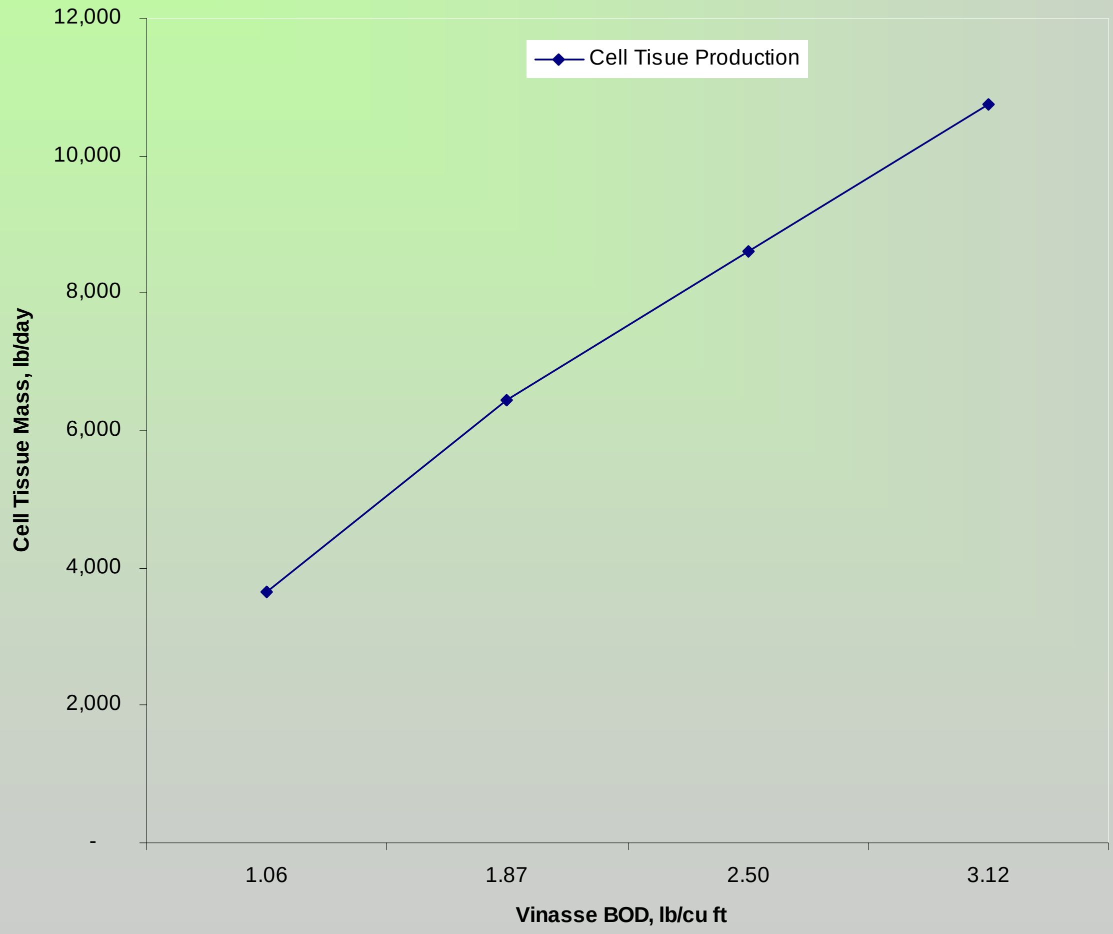
Results Discussion (Cont.)

- For high-rate digesters the volumetric loading rate ranges from 0.10 to 0.48 lb/cu ft day (Metcalf & Eddy, Inc., 1991), however mixing problems occur beyond 0.30 lb/cu ft day.

Results Discussion (Cont.)

Influent vinasse BOD, mg/l	Net Mass of Cell Tissue (Px), lb/day
17,000	3,658
30,000	6,455
40,000	8,606
50,000	10,758

Mass of Cell Tissue Produced



Gas-BOD Reacted Ratio

	Gas production/weight of volatile solids destroyed, l/mg	Gas production/weight of volatile solids destroyed, cu ft/lb
Influent vinasse BOD, mg/l		
17,000	0.56	8.92
30,000	0.56	8.92
40,000	0.56	8.92
50,000	0.56	8.92

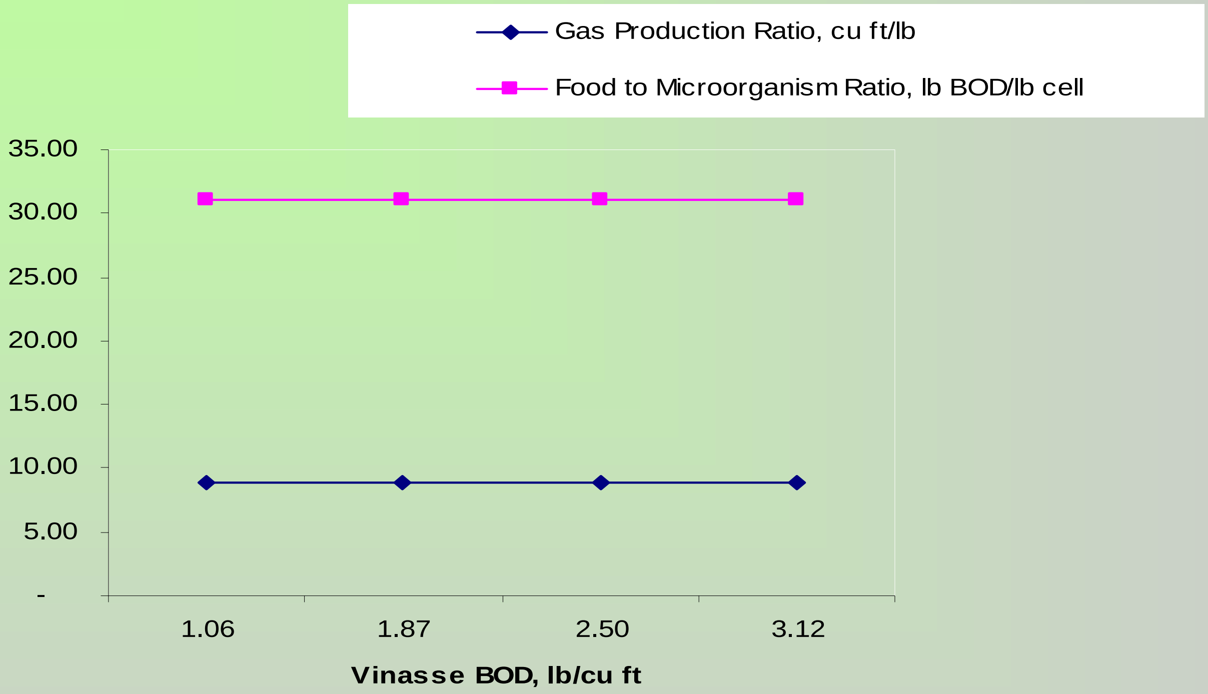
Results Discussion (Cont.)

- The volume of gas produced from each each pound of BOD destroyed ranges from 8 to 18 cu ft/lb (Metcalf & Eddy, Inc., 1991), which is in agreement with model calculated value of 8.92 cu ft/lb

Food to Microorganism Ratio

	Food to Microorganisms ratio, mg BOD/mg cell mass
Influent vinasse BOD, mg/l	
17,000	31.03
30,000	31.03
40,000	31.03
50,000	31.03

Food to Microorganism Ratio (Cont.)



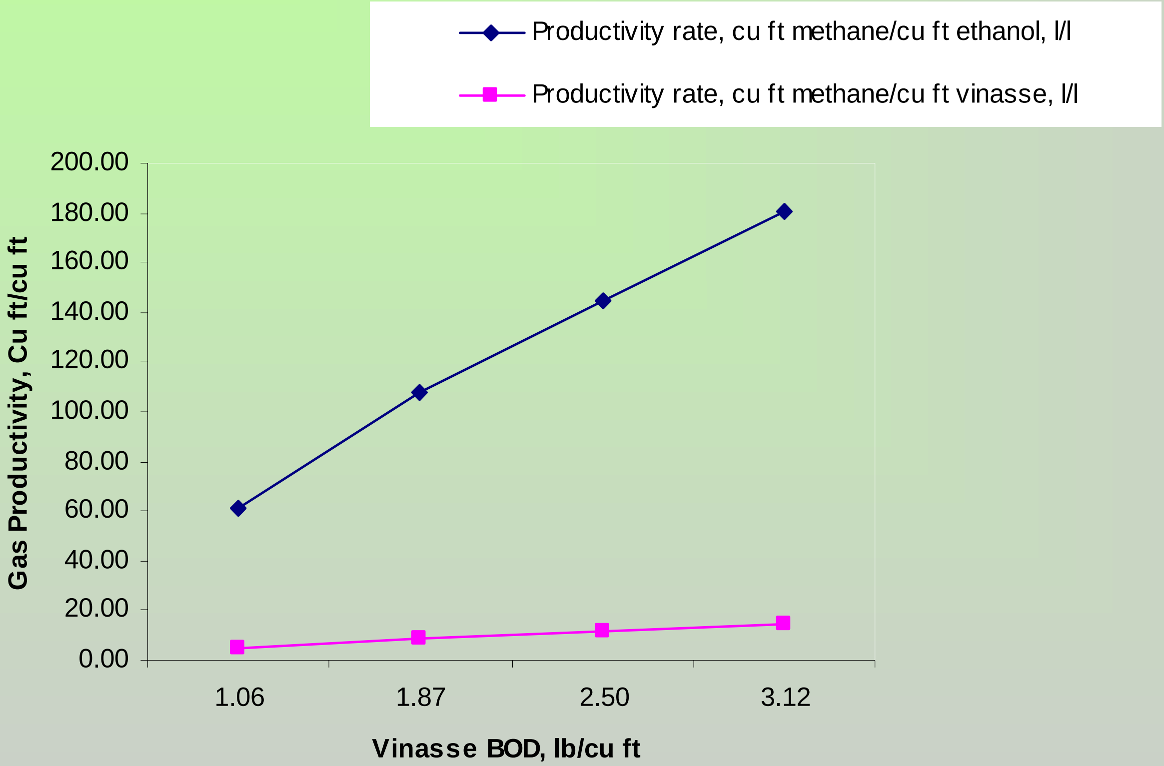
Results Discussion (Cont.)

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

Methane to Vinasse Productivity

Influent vinasse BOD, mg/l	Productivity rate, cu ft methane/cu ft ethanol, l/l	Productivity rate, cu ft methane/cu ft vinasse, l/l
17,000	61.31	5.11
30,000	108.19	9.02
40,000	144.26	12.02
50,000	180.32	15.03

Methane to Vinasse Productivity



Recommendations

- Conduct a feasibility study of vinasse anaerobic digestion to evaluate the process economics
- Scrub the methane to pipeline-specs natural gas and inject it into the existing natural gas distribution grid for great payback to the distillery
- Use the ammonia produced in the ethanol fermentation process

Recommendations

- Further process the digested vinasse effluent to produce even greater value-added products in the sugar distillery:
  - potable water and
  - either liquid or solid fertilizers
  - Animal feed

Famous Quote

"We may rest assured that as green plants and animals disappear one by one from the face of the globe, some of the fungi will always be present to dispose of the last remains"

- B.O. Dodge