

## PILOT-SCALE DISTILLERY SPENTWASH BIOMETHANATION

By P. P. Karthadkar,<sup>1</sup> B. K. Handa,<sup>2</sup> and P. Khanna<sup>3</sup>

**Abstract:** Mesophilic biomethanation of distillery spentwash has been investigated at a pilot scale with a diphasic anaerobic process. An operational strategy to suppress sulfide inhibition through pH control in the methane phase has also been validated. The acid phase has been operated on lime-neutralized spentwash at an organic loading rate of 30 kg COD/m<sup>2</sup>/day. Methane phase operation without solids recycling enabled 65% COD reduction and 0.3 m<sup>3</sup> of biogas production with 60% methane per kilogram COD utilized at an organic loading rate of 3.25 kg COD/m<sup>2</sup>/day. The contact methane phase at 5 kg COD/m<sup>2</sup>/day and 27 day mean cell-residence time achieved 70% COD reduction and 0.3 m<sup>3</sup> gas production with 70% methane per kilogram of COD utilized. An energy audit revealed over 13 times the energy production per unit energy consumed in the process. A mathematical model for the acid phase predicted volatile acid concentrations within 15% of experimental results. The methane phase model incorporated inhibition and was independent of growth or nongrowth associated phenomena. The model predicted effluent substrate concentrations and gas yields within 10% and 15% of experimental values in the methane phase, respectively.

### INTRODUCTION

With major constituents of carbohydrates and minerals, distillery spentwash from molasses fermentation is characterized, as shown in Table I, by high biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), low pH, high temperature, high dissolved solids, and high concentrations of inorganics. Such spentwash warrants extensive treatment before disposal. Anaerobic processes enabling recovery of biogas appear to offer the most appropriate treatment options if the systems can be designed and operated for the prevailing high concentrations of soluble organics and ions in the spentwash.

Theoretically, various process alternatives in anaerobic digestion, from lagoons to fixed-film reactors, can be used for biomethanation of distillery spentwash (Karthadkar 1988). Among these, the diphasic anaerobic process seems most appropriate for high-strength spentwash, because of its widely reported advantages (Cohen et al. 1979; Ghosh and Pohland 1974; Massey and Pohland 1978), e.g., the possibility of maintaining optimal environmental conditions for the acid- and methane-forming organisms, attenuation of imbalances between organic acid production and consumption, stable performance, and a high methane content in the biogas produced in this process.

Extensive bench-scale studies have been performed on the diphasic anaerobic contact process preceded by lime neutralization and heat recovery for distillery spentwash (Agharkar 1983; Karthadkar 1983; Patnaik 1984; Rahman 1984). The optimum hydraulic retention time (HRT) of 1.2 days in the

$Q$	=	raw wastewater flow (L/day);
$Q_r$	=	sludge recycle rate (L/day);
$Q_w$	=	sludge wastage flow rate (L/day);
$Q_{rw}$	=	sludge recycle rate (L/day);
$R$	=	net biomass growth rate (mg/L-day);
$r_k$	=	substrate utilization rate (mg/L-day);
$r_s$	=	steady-state effluent substrate concentration (mg/L);
$S$	=	influent substrate concentration (mg/L);
$S_0$	=	critical substrate concentration (mg/L);
$S^*$	=	volume of the aeration tank (L);
$V$	=	biomass concentration in aeration tank (mg/L);
$X$	=	biomass concentration in effluent (mg/L);
$X_e$	=	biomass concentration in recycle (mg/L);
$X_r$	=	cell yield (g VSS formed/g substrate used);
$Y$	=	mean cell residence time (days);
$\theta_c$	=	critical mean cell residence time (days);
$\theta_c^*$	=	geometric mean critical cell residence time (day);
$\theta_c^*$	=	hydraulic detention time (days);
$\theta_h$	=	specific growth rate (days <sup>-1</sup> ); and
$\mu_m$	=	maximum attainable growth rate (days <sup>-1</sup> ).

<sup>1</sup>CSIR Fellow, Nat. Envir. Engrg. Res. Inst., Nehru Marg, Nagpur 440 020, India.

<sup>2</sup>Deputy Dir., Nat. Envir. Engrg. Res. Inst., Nehru Marg, Nagpur 440 020, India.

<sup>3</sup>Dir., Nat. Envir. Engrg. Res. Inst., Nehru Marg, Nagpur 440 020, India.

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**TABLE 1. Characteristics of Molasses-Based Distillery Spentwash**

Sample number (1)	Characteristics (2)	Range (g/L) (3)	Average (g/L) (4)
1	pH	4.33-4.55	4.4
2	Temperature (°C)	95-105	98.0
3	Total solids	90.5-105.9	97.0
4	Volatile solids	41.5-55.8	49.3
5	Suspended solids	3.4-5.6	4.2
6	Ash	47.4-56.1	52.4
7	TVA as acetic acid	2.9-3.53	3.2
8	Total nitrogen	1.2-3.0	2.1
9	Sodium as Na	1.4-3.0	2.7
10	Potassium as K	9.1-10.0	9.5
11	Calcium as Ca	1.2-2.7	2.2
12	Phosphorus as P	0.043-0.29	0.15
13	Sulfate as SO <sub>4</sub>	1.1-3.0	2.5
14	COD	102-130	115.8
15	BOD <sub>5</sub>	55-65	59.4
16	TC	60-70	63.9
17	TOC	45-55	48.3
18	TOD	125-140	133.7
19	Glucose	—	13.5
20	Fructose	—	12.5

acid phase with an organic loading rate (OLR) of 58 kg COD/m<sup>3</sup>/day (Karahadkar 1983), as well as an HRT and a mean cell residence time (MCRT) of 17 days and 40 days, respectively, in the methane phase an OLR of 3.2 kg COD/m<sup>3</sup>/day, resulted in 70% COD reduction with biogas production of 0.27 m<sup>3</sup>/kg of COD utilized (60% methane content) during bench-scale studies (Patnaik 1984; Raman 1984).

Distillery spentwash contains of K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions at concentrations reportedly inhibitory to methanogens. A series of toxicity assays on inhibition of methanogenesis with synthetic spentwash containing different concentrations of K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> indicated that SO<sub>4</sub><sup>2-</sup> ions, rather than K<sup>+</sup>, limit the methanogenesis (Karahadkar et al. 1987). The toxic effect of K<sup>+</sup> was attenuated by the acclimation of microorganisms to K<sup>+</sup> and the antagonistic effect caused by Ca<sup>2+</sup> and Na<sup>+</sup> (Kungelman and Chin 1971). Further, sulfide toxicity was observed to be directly proportional to H<sub>2</sub>S concentration, [H<sub>2</sub>S], in the gas. Because the [H<sub>2</sub>S] in the gas can be controlled by enhancing the pH of the methane phase to 7.7 or above, the pH control can constitute a process-control strategy for suppression of sulfide inhibition (Karahadkar et al. 1987).

These results for a bench-scale diphasic anaerobic process in biomethanation of distillery spentwash prompted the present investigation with a view to validating its feasibility with respect to its operational performance and its energy balance.

Most modeling endeavors on biomethanation have been based on the assumption of growth-associated product formation (Bhatia et al. 1985b). Monod's equation and its derivatives have been used to model anaerobic processes. However, Monod's equation is based on growth association and

does not account for inhibition. The difficulty encountered in the present study in comprehending the performance of the methane phase based on such formulations has encouraged the writers to seek alternative models with the specific objective of developing a simple tool to predict the performance of the process.

## MATERIALS AND METHODS

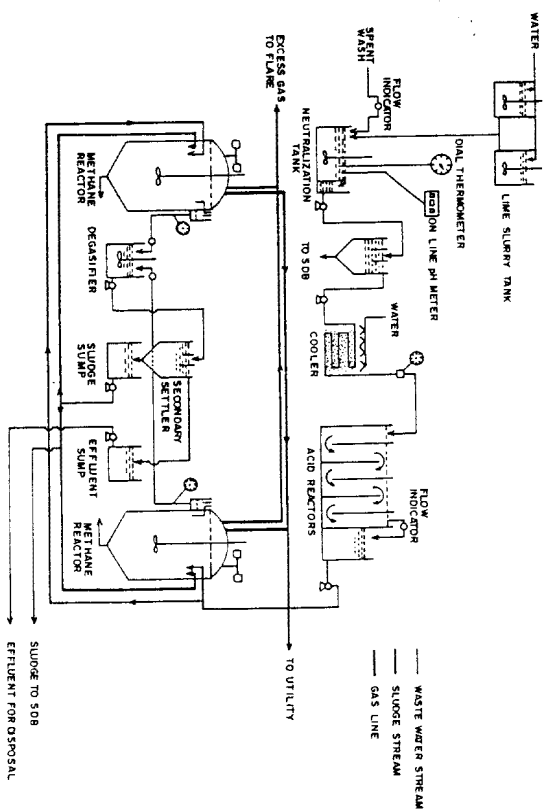
### Pilot Plant

The pilot plant was located in a distillery at Nira, Maharashtra, India. The plant processes depicted schematically in Fig. 1, consist of three distinct steps: neutralization of spentwash, an acid phase, and a methane phase. The acid phase comprises two open horizontal plug flow reactors, each of 30 m<sup>3</sup> capacity. The methane phase consists of two closed vertical continuously stirred tank reactors (CSTRs), each of 160 m<sup>3</sup> capacity. The plant incorporates process-control aids such as heat recovery from raw spentwash, on-line pH meters, thermometers, and flow indicators. Necessary gas collection, utilization, and flare facilities have also been installed.

Distillery spentwash, following neutralization to pH 6.0 with lime and heat recovery, enters the acid phase with a temperature of 45° C. The organic acid-rich spentwash from the acid phase is charged to the methane phase from a secondary settler, where solids are separated, and then recycled to the methane phase. The influent spentwash flow rates have been regulated to provide desired HRTs in various units.

### Sampling and Analyses

Grab samples were withdrawn directly from the reactors for time-sensitive parameters like pH, volatile acids, and alkalinity, and analyzed once per day.



**FIG. 1. Schematics of Pilot Plant for Diphasic Biomethanation of Distillery Wastewater**

For other parameters, composited samples averaged over a day were used in the analyses. COD, sulfate, sulfide, and phosphate were estimated twice a week, whereas solids were analyzed three times in two weeks. Cations and total Kjeldahl nitrogen (TKN) were analyzed once a week. BOD<sub>5</sub> (biochemical oxygen demand at five days and 20° C) was estimated occasionally. All these analyses were carried out in conformity with the standard methods (APHA, AWWA, and WPCF 1976). Total carbon (TC), total organic carbon (TOC), and total oxygen demand (TOD) values were estimated occasionally from analyses with an Ionics 1270 TC/TOC/TOD analyser. The CH<sub>4</sub> and CO<sub>2</sub> concentrations in the biogas were estimated daily through gas chromatography using a Poropak Q 80-100 column and Perkin-Elmer SIGMA 3B gas chromatograph at a temperature of 110° C, with a thermal conductivity detector maintained at a temperature of 200° C and an H<sub>2</sub> carrier gas rate of 40–50 ml/min.

#### Reactor Start-Up

The cultures for start-up of the acid and methane reactors were developed from bench-scale reactors employing the techniques of seed collection, propagation, and start-up delineated by Szendrey (1984). The start-up processes were completed within one to 10 weeks for the acid and methane phases, respectively.

#### Scheme of Operation

Undiluted distillery spentwash was used in the process throughout the study. The acid phase was operated in a once-through flow mode. The methane phase was operated in two different modes to enable comparison of reactor performance with and without solids recycling.

### RESULTS

#### Influent Characteristics

Routine analyses of the spentwash revealed substantial variation, as given in Table 1, due to frequent changes in sources of molasses at the distillery.

The temperature of the spentwash was brought down from 95–105° C to 50–55° C, enabling substantial heat recovery prior to neutralization. The neutralized spentwash was cooled further to 43–47° C, thereby ensuring that the temperatures of the acid and methane phases prevailed in the ranges of 40–44° C and 31–35° C, respectively.

#### Acid Phase

The representative steady-state performance of the acid phase in the OLR range of 19–34 kg COD/m<sup>3</sup>/day is shown in Fig. 2. The increase in total volatile acid (TVA) concentration from an average value of 2.56 g/L in the influent to an average value of 15.76 g/L in the effluent demonstrates the efficacy of the acid phase at pH and alkalinity values above 6.0 and 9.0 g/L, respectively.

The decrease in the acid-phase effluent TVA concentration to 11.7 g/L as a result of a reduction in pH and alkalinity values to 5.7 and 6.3 g/L did not agree with earlier bench-scale results (Agharkar 1983; Karhadkar 1983), wherein the TVA concentrations in the acid-phase effluent were observed to be 13–22 g/L at a pH range of 5.6–5.8. This variation could be attributed

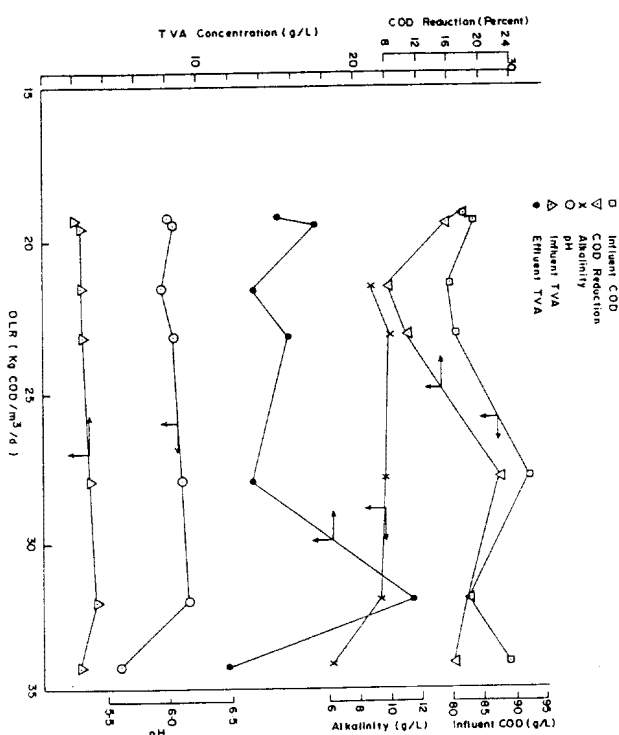


FIG. 2. Performance of Acid Phase at Different OLRs

to the substantial change in composition of spentwash during bench- and pilot-scale studies (e.g., 70–80 and 115.8 g/L COD, respectively). The OLR in the acid phase was restricted to 30 kg COD/m<sup>3</sup>/day in the pilot-scale studies, thereby maintaining the pH and alkalinity values above 6.0 and 9.0 g/L, respectively, in keeping with the performance data in Fig. 2.

#### Methane Phase without Recycling

The representative steady-state performance of the methane phase without recycling at different OLRs in the range of 0.7–5.0 kg COD/m<sup>3</sup>/day is shown in Figs. 3(a and b). At all the OLRs, despite a fluctuating influent COD to the methane phase, COD reduction efficiencies of over 64% were achieved in the methane phase. Biogas production was proportional to total COD utilized, with a yield of 0.3 m<sup>3</sup>/kg COD utilized and an average methane content of 60%.

With the increase in organic loading rate, TVA concentration increased from 7.5 to 12 g/L [Fig. 3(b)], while the TVA/alkalinity ratio increased from 0.62 to 0.75. This signifies a build-up of buffering capacity in the methane phase, enabling maintenance of the pH of the reacting liquor in the methane phase above 7.7. This is deemed necessary to control the concentration of free sulfides and, in turn, sulfide toxicity to methanogenesis (Karhadkar et al. 1987).

A strong positive correlation of effluent substrate concentration with sulfide concentrations in the liquid and gas, as evidenced by data presented in Table 2, indicates that sulfide-related inhibition of the methanogenesis agrees well with the observations made during the bench-scale studies of Karhadkar et al. (1987). Koster et al. (1986) also supported sulfide inhibition of meth-

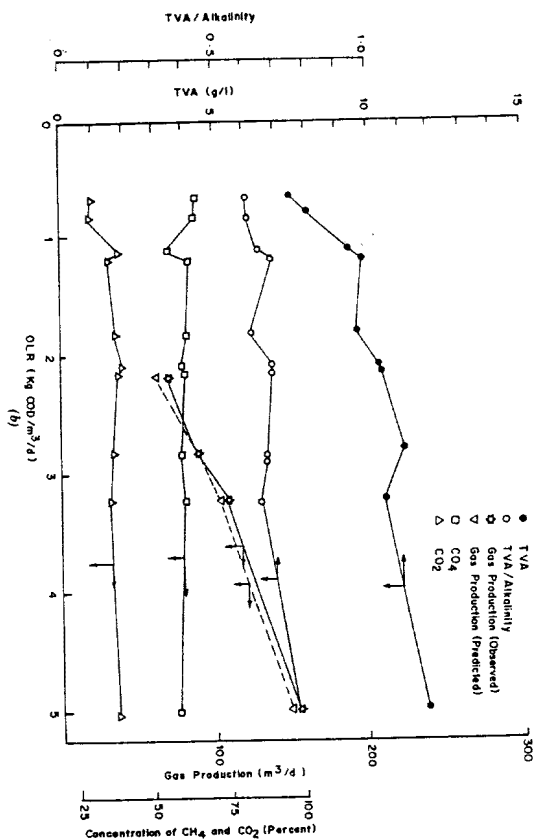
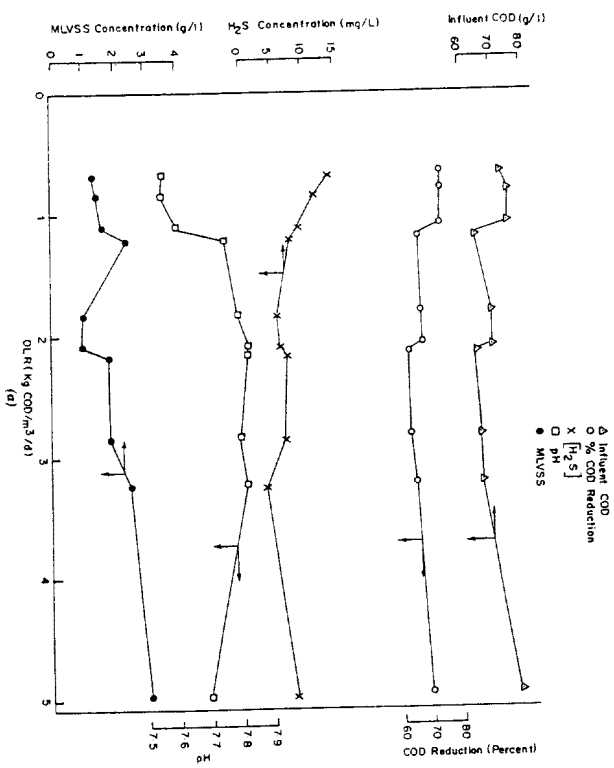


FIG. 3. Performance of Methane Phase without Recycling: (a) Influent COD, COD Reduction, pH, MLVSS, and  $[H_2S]$  in Gas; (b) TVA, TVA/Alkalinity, Gas Production, and  $CH_4$  and  $CO_2$  Concentrations

anogenesis and correlated the degree of inhibition in the pH range of 7.55–7.85 to total sulfide, not to free sulfide. The correlation coefficient of 0.714 for  $S^{2-}$  with  $[H_2S]$  in the gas suggests a dominance of un-ionized sulfide-related inhibition. Hilton and Oleszkiewicz (1988) observed that methano-

TABLE 2. Correlation Matrix for Methane Phase without Recycling

Variable (1)	Influent substrate concentration, $S_0$ (2)	Effluent substrate concentration, $S$ (3)	Hydraulic retention time (4)	Total $S^{2-}$ in liquid (5)	$[H_2S]$ in gas (6)
$S_0$	1	0.5328	0.2670	0.2770	0.8510
$S$	0.5328	1	-0.4763	0.8369	0.7136
HRT	0.2670	-0.4763	1	-0.6007	0.1404
Total $S^{2-}$	0.2770	0.8369	-0.6007	1	0.5166
$[H_2S]$	0.8510	0.7136	0.1404	0.5166	1

genesis is affected directly by high concentrations of un-ionized  $H_2S$ , and they concluded that the carbon-removal process is through the methanogenic pathway in the presence of high pH and total sulfide. This pilot study lends support to their conclusion.

The prolonged observations in the operation of the methane phase without recycling indicated a high susceptibility of methanogenesis to temperature shocks and organic overloadings. Such process upsets were overcome with a maximum OLR of 3.25 kg COD/ $m^3$ /day, enabling stable performance with an average COD reduction efficiency of 65% and a gas yield of 0.3  $m^3$ /kg COD utilized (60% methane).

#### Contact Methane Phase

Initial trials to operate a methane phase as a contact process were unsuccessful due to poor solids separation efficiency caused by a low concentration (1.96 g/L) of mixed liquor volatile suspended solids (MLVSS) in the methane reactors. Addition of an organic flocculant in the influent to the methane reactors increased the MLVSS concentration to 6 g/L in four weeks. Subsequent discontinuation of flocculant addition allowed the MLVSS concentration to be maintained without assistance at levels high enough (5.8 g/L) to enable sustained operation of the methane phase as a contact process.

The contact process was operated at three values of the MCRT, and results of its steady-state performance are shown in Table 3 and Figs. 4(a and b). The contact methane reactor exhibited stable performance at an OLR of 5 kg COD/ $m^3$ /day and an MCRT of 27 days. Despite fluctuating influent COD values and  $H_2S$  concentrations in the gas: COD, TOD, BOD, TC, and TOC reduction efficiencies at an MCRT of 27 days were recorded as 70%, 64%, 81%, 67%, and 78%, respectively, through the methane phase, and 77%, 76%, 86%, 77%, and 85%, respectively, over the entire process. The gas yield in the contact methane phase has been comparable to that in a methane phase without recycling. However, the gas contained 70% methane in the contact mode operation due to higher MCRT and MLVSS values, and that minimized the effect of sulfide inhibition on methanogenesis compared to 60% methane in the methane phase without recycling.

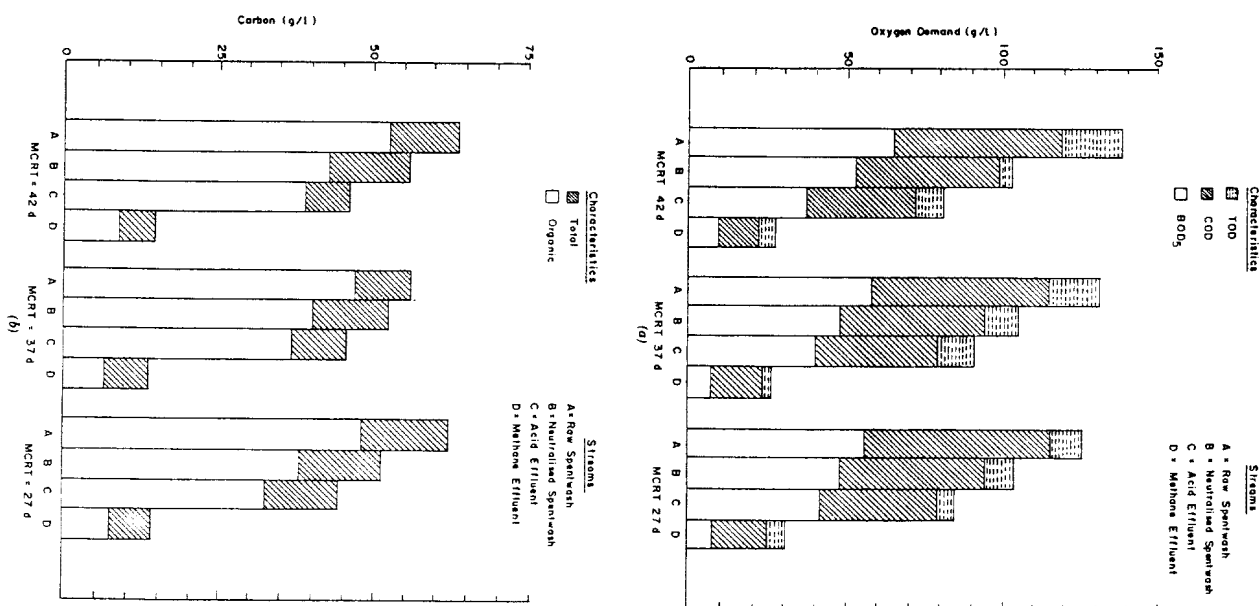
The lower efficiency of organics removal (68% in terms of COD) in the methane phase at 42 day MCRT in comparison to 37 and 27 day MCRT's (71% and 70%, respectively) could be attributed to a higher  $H_2S$  concentration (8 mg/L) in the gas due to a lower pH (7.59) of the mixed liquor. This was caused by a sudden drop in ambient temperature, which resulted in an

TABLE 3. Performance of Contact Methane Phase

Sample number (1)	Parameter (2)	Set I		Set II		Set III	
		Range (3)	Average (4)	Range (5)	Average (6)	Range (7)	Average (8)
1	HRT (days)	—	20	—	16	—	16
2	MCRT (days)	40–45	42	34–38	37	26–31	27
3	Q (m <sup>3</sup> /day)	—	8	—	10	—	10
4	OLR (kg COD/m <sup>3</sup> /day)	3.55–3.72	3.66	4.60–5.57	4.98	4.85–5.13	5.00
5	pH	7.50–7.65	7.59	7.75–7.85	7.78	7.75–7.85	7.77
6	TVA (g/L)						
	Influent	15.70–17.76	16.6	14.5–18.4	15.7	16.0–17.5	16.8
	Effluent	7.4–10.7	9.1	7.7–11.4	8.8	10.2–12.9	11.3
7	TVA/alkalinity	0.54–0.70	0.68	0.60–0.70	0.64	0.60–0.70	0.65
8	MLVSS (g/L)	4.5–6.5	5.5	4.2–6.1	5.2	4.6–6.8	5.7
9	Sulfide (g/L)	0.60–0.77	0.69	0.55–0.70	0.63	0.57–0.72	0.65
10	Q <sub>gas</sub> (m <sup>3</sup> /day)	115–127	121	176–185	179	164–171	169
11	Gas yield (m <sup>3</sup> /kg COD)	—	0.301	—	0.321	—	0.308
12	Predicted gas yield (m <sup>3</sup> /day)	—	142.8	—	175.2	—	156.6
13	Difference in predicted and observed gas yields (%)	—	15	—	2.1	—	7.9
14	Gas composition (%)						
	CH <sub>4</sub>	65.0–71.0	68.3	68.0–71.0	70.2	68.0–71.0	70.1
	CO <sub>2</sub>	25.0–31.0	29.7	25.0–28.0	26.5	25.0–28.0	26.7
	H <sub>2</sub> S	6–11	8.0	2–6	4.6	3–8	5.0

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FIG. 4. Performance of Contact Methane Phase: (a) TOD, COD, and BOD<sub>5</sub>; (b) TC and TOC



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TABLE 4. Comparison of Anaerobic Processes for Treatment of Distillery Spentwash (Karhadkar 1988)

Analysis number (1)	Process/reactor (2)	Temperature <sup>1</sup> (°C) (3)	Volume <sup>2</sup> (L) (4)	HRT (days) (5)	OLR (kg COD/m <sup>3</sup> /day) (6)	COD (g/L) (7)	SO <sub>4</sub> (g/L) (8)	(COD/SO <sub>4</sub> ) (9)	Cod reduction efficiency (%) (10)	Total COD reduction efficiency <sup>3</sup> (%) (11)	Gas production, GPV <sup>4</sup> volumetric (m <sup>3</sup> /m <sup>3</sup> reactor/day) (12)	Gas Composition		
												CH <sub>4</sub> (%) (13)	CO <sub>2</sub> (%) (14)	H <sub>2</sub> S (mg/L) (15)
1	Semi-CSTR	35	4	10	3.2	32	2.9	11.0	96	—	2	59	38	—
2	Series-CSTR	—	10	10	6.8	65	—	—	91	—	2.4	49	—	—
3	CSTR	55	4	80	0.4	30	6.8	4.4	62	—	1.8	62	37	—
4	CSTR	33	4	50	0.25	12	5.8	2.1	43	—	1.5	54	45	—
5	Contact	35	—	—	—	62	7.5	8.3	—	—	0.3	—	—	—
6	Contact	—	640	16	1.7	28	0.1	280	68	—	2.5	52	43	1
7	Contact	—	—	6.2	4.0	25	2-5	5-12	95	—	—	58	40	—
8	Contact	33	—	3.8	9.0	13	—	—	70	—	—	—	—	—
9	Contact	35	30	6.5	8.5	55	1.3	42.3	83	—	5.2	56	—	—
10	Contact	—	20	35	1.8	70-100	3-5	20-30	71	—	0.8	56	—	—
11	Contact	—	1,890	25	3.2	70-100	3-5	20-30	70	—	1.1	62	37	—
12	Diphasic contact	37	5	16	3.31	53	—	—	42	—	0.9	—	—	—
13	Filter	—	365	30	3.3	99	—	—	64	—	—	—	—	—
14	Filter	35	7,540	10.5	4.9	50	—	—	81	—	1.9	62	—	—
Present study	Plug flow acid	45	3 × 10 <sup>4</sup>	2.6	32	83	1.7	48.8	14	—	—	—	—	—
	CSTR-methane	33	1.6 × 10 <sup>4</sup>	20	3.5	72	1.4	51.4	66	79	0.7	61	36	4.5
Present study	Plug flow acid	45	3 × 10 <sup>4</sup>	2.6	36	95	1.7	55	16	—	—	—	—	—
	Contact-methane	33	1.6 × 10 <sup>5</sup>	16	5.0	80	1.4	57	70	80	1.1	70	27	5

<sup>3</sup>Calculated on the basis of average spentwash COD of 115.8 g/L.

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imbalance in volatile acid production and consumption. The drop in pH has also been associated with increased free-sulfide production (shown by a high H<sub>2</sub>S concentration in the gas) and concomitant enhanced inhibition of methanogenesis. The situation was retrieved by increasing the pH in the methane phase by internal buildup of buffering capacity through an increase in the MCRT and/or a reduction of the OLR. The direct alkali addition was not adopted due to the resultant buildup of undesirable ionic constituents in the methane phase.

An extensive performance review of various anaerobic processes, including the present investigation, for the biometanation of distillery spentwash is presented in Table 4. The COD reduction efficiency of 80% over the entire process at an OLR of 5 kg COD/m<sup>3</sup>/day achieved in the contact process of the present study compares well with the reported performances (analyses 10 and 11 in Table 4) for spentwash with comparable COD values.

The energy audit for the contact process in this study revealed that the contact process recovered (heat and biogas) energy of 0.569 MJ/kg of spentwash against an expenditure of 0.042 MJ/kg of spentwash, thus generating more than a 13.5-fold increase in energy per unit of energy consumed in the process.

**MATHEMATICAL MODELING**

Even with high organics-removal efficiencies and biogas yields at high OLRs, there was no discernible increase in MLVSS concentrations in the methane phase during the course of the present pilot-scale study. The high rate of product formation thus appears possible without cell synthesis, contrary to the classical assumption of growth-associated methanogenesis. This theory contends that the increase in substrate concentration enhances the cell growth rate with a concomitant increase in energy consumption and substrate utilization or product formation. Bhatia et al. (1985a) have also questioned the premise of growth association in methanogenesis. These researchers (Bhatia et al. 1985b) argue that the extent of methanogenesis is proportional to total energy E<sub>T</sub> transfer, and anything that increases E<sub>T</sub> (either growth or maintenance) should enhance methane production. Most of the carbon accounted for by E<sub>T</sub> in methanogenesis is used for gas production; only a small fraction contributes to the production of cellular mass.

Since the maintenance energy requirement is directly proportional to the ionic strength of the reacting liquor, maintenance energy is expected to account for a substantial part of E<sub>T</sub> in the case of distillery spentwash due to its high concentrations of ash and ions. Therefore, only a small fraction of energy is available for cell synthesis. High gas-production rates in the present investigation occurred as the result of an increase in maintenance energy, which supports the contention put forth by Bhatia et al. (1985b).

**Model for Acid Phase**

The formulation describing product concentration, delineated by Ghosh and Pohland (1974), has been found to model TVA concentration satisfactorily in this research. Accordingly

$$P = \frac{\alpha_p(U_c + m\theta)(S_p - S)}{(U_p + U_c + m\theta)} \dots \dots \dots (1)$$

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where  $P$  = steady-state product concentration ( $\text{ML}^{-3}$ );  $\alpha_p$  = product yield coefficient;  $U_p$  and  $U_c$  = substrate-utilization coefficients for synthesis and energy, respectively;  $m$  = maintenance energy coefficient ( $\text{T}^{-1}$ );  $\theta$  = HRT ( $\text{T}$ ); and  $S_o$  and  $S_e$  = influent and effluent substrate concentrations, respectively.

The merit of this equation lies in its underlying assumption that liquid and gaseous end products are derived from substrate fractions catabolized for the production of energy required for synthesis and maintenance. This agrees with the principles of nongrowth-associated product formation (Pirt 1975). Further, the total biochemical substrate assimilation process is represented by two substrate-utilization coefficients,  $U_p$  and  $U_c$ .

COD and TVA estimated as acetic acid have been associated with substrate and product in the acid phase, respectively. As one mole of acetic acid (60 g) exerts a COD value of 64 g, the COD contribution per gram of acetic acid is 1.067 g. The available substrate COD for acid-formers, accordingly, can be estimated by subtracting the COD contributed by TVA from the total COD values.

The parameters in Eq. 1 have been estimated from data presented in Fig. 2 through regression analysis, by the method put forth by Ghosh and Pohland (1974), as  $U_p = 3.129$ ;  $U_c = 0.207$ ;  $\alpha_p = 3.91$ ; and  $m = 0.1228$ .

Assuming the TVA concentration in the influent to the acid phase is negligible, the steady-state product yield  $P$  could be expressed as follows:

$$P = \frac{\beta_p}{(1 - 1.067\beta_p)} (\text{COD}_o - \text{COD}) \quad \dots \dots \dots (2a)$$

where

$$\beta_p = \frac{P(U_c + m\theta)}{(U_p + U_c + m\theta)} \quad \dots \dots \dots (2b)$$

$\beta_p$  is a function of HRT for a given system; therefore, for a fixed value of HRT, Eq. 2 reduces to a straight line passing through the origin with a slope of  $\beta_p/(1 - 1.067\beta_p)$ . Fig. 5 shows Eq. 2 as a series of straight lines for different values of HRT. The values of  $P$  have been predicted for a priori fixed HRTs in the acid and compare within 15% of the observed values, despite underlying assumptions in the model regarding acetic acid as the sole product of the acid phase and negligible TVA concentration in the influent to the acid phase.

**Model for Methane Phase**

According to Bhaita et al. (1985b), substrate utilization could be expressed by the following equation:

$$\text{SUR} = \frac{RS}{(1 + K_s \cdot S)(1 + K_i \cdot I)} \quad \dots \dots \dots (3)$$

where  $\text{SUR}$  = substrate-utilization rate ( $\text{ML}^{-3} \text{T}^{-1}$ );  $R$  = maximum rate of substrate utilization ( $\text{T}^{-1}$ );  $K_s$  = substrate-affinity coefficient ( $\text{M}^{-1} \text{L}^3$ );  $K_i$  = inhibition coefficient ( $\text{M}^{-1} \text{L}^3$ ); and  $I$  = inhibitor concentration ( $\text{ML}^{-3}$ ). In the present case, COD has been assumed to be the sole substrate, and

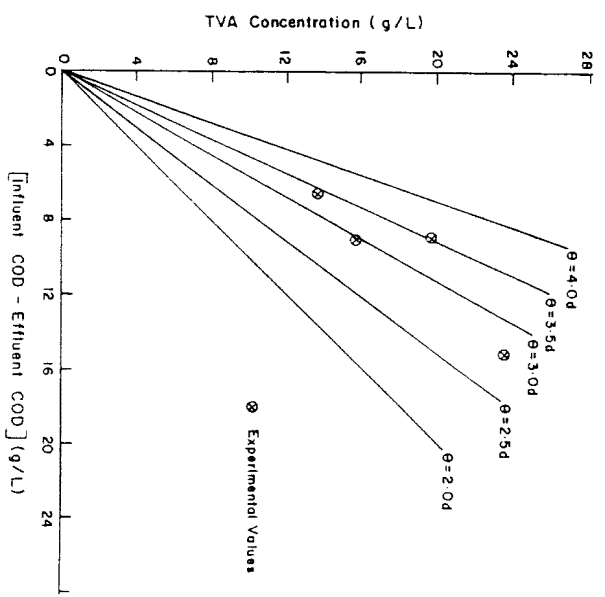


FIG. 5. Observed and Predicted TVA Concentrations in Acid Phase

$\text{H}_2\text{S}$  concentration in the gas accounts for sulfide inhibition. With these assumptions, Eq. 3 could be presented as follows:

$$\text{SUR} = \frac{RS}{(1 + K_s S)(1 + K_i [\text{H}_2\text{S}])} \quad \dots \dots \dots (4)$$

where  $[\text{H}_2\text{S}]$  =  $\text{H}_2\text{S}$  concentration in gas ( $\text{ML}^{-3}$ ); and  $K_i$  = a coefficient related to sulfide inhibition ( $\text{M}^{-1} \text{L}^3$ ).

The SUR at steady state can be represented by  $(S_o - S)/\theta$ . The values of  $R$ ,  $K_s$ , and  $K_i$  have been estimated using an optimization technique with recourse to an internal penalty function to minimize (observed  $S - \text{calculated } S$ )<sup>2</sup> for the data presented in Fig. 3(a) with respect to the methane phase without recycling as 1.906 per day, 0.00116 L/g, and 5.091 L/mg, respectively. Putting  $K_s = 0$ , Eq. 4 at steady state can be expressed as follows:

$$\frac{S_o - S}{\theta} = \frac{RS}{(1 + K_i [\text{H}_2\text{S}])} \quad \dots \dots \dots (5)$$

Eq. 5 leads to an explicit expression for  $S$  as follows:

$$S = \frac{S_o}{\left( \frac{1}{\theta} + \frac{R}{1 + K_i [\text{H}_2\text{S}]} \right)} \quad \dots \dots \dots (6)$$

Fig. 6 shows the relationships for  $S$  as a function of  $[\text{H}_2\text{S}]$  by substituting estimated values of  $R$  and  $K_i$  and observed values of  $S_o$  and HRT into Eq. 6. The predicted values of  $S$  fall within 10% of observed values.

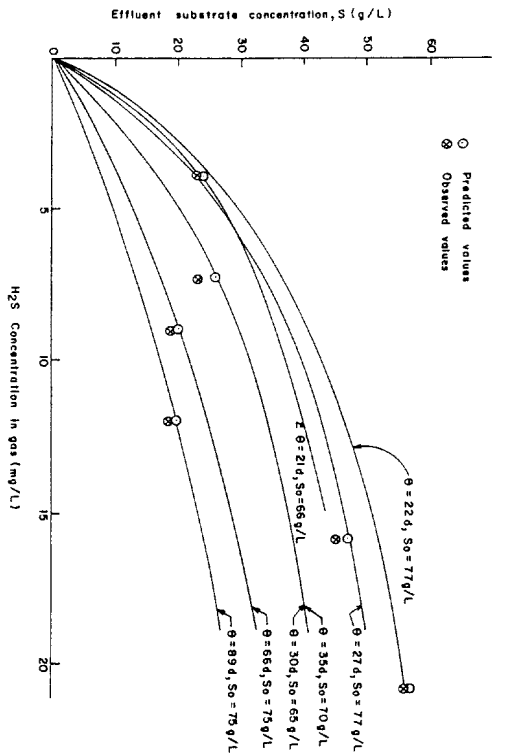


FIG. 6. Observed and Predicted Effluent Substrate Concentrations in Methane Phase without Recycling

The effluent substrate concentration  $S$  in the contact methane phase has also been predicted employing Eq. 6 with a modified  $K_f$ . The modification takes into account the ability of the process to withstand the sulfide-inhibition effect. The value for  $K_f$  in the contact methane phase  $K_{fC}$  could be expressed as follows:

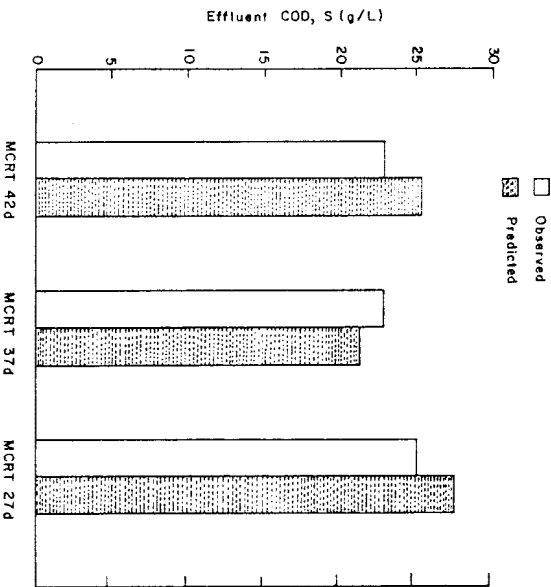


FIG. 7. Observed and Predicted Effluent Substrate Concentrations in Contact Methane Phase

$$K_{fC} = K_f \cdot \left( \frac{\theta_c}{\theta_c} \right) \dots \dots \dots (7)$$

where,  $\theta_c =$  MCRRT in the contact methane phase (T). Incorporating Eq. 7 into Eq. 6,  $S$  for the contact methane phase has been calculated, and is shown in Fig. 7. The predicted values of  $S$  lie within 10% of observed values.

The values of  $S_0$  and  $S$  provide the quantity of substrate utilized per unit volume, which in turns leads to the estimation of gas production. This has been expressed by the following equation:

$$Q_{\text{gas}} = GQ(S_0 - S) \dots \dots \dots (8)$$

where  $Q_{\text{gas}} =$  gas-production rate ( $L^3 T^{-1}$ );  $Q =$  hydraulic flow rate ( $L^3 T^{-1}$ ); and  $G =$  a conversion constant ( $M^{-1} L^3$ ).

In both the methane phases, i.e., with and without recycling, the value of  $G$  was observed to be  $0.3 \text{ m}^3/\text{kg}$  COD utilized. The predicted gas yield values are shown in Fig. 3(b) for the methane phase without recycling and in Table 3 for the contact methane phase. The predicted values of  $Q_{\text{gas}}$  lie within 15% of observed values.

**CONCLUSIONS**

The results presented in this study demonstrate the feasibility of diphasic anaerobic processes for the biomethanation of distillery spentwash at a pilot scale. The methane phase without recycling could operate on a sustainable basis at an OLR of  $3.25 \text{ kg COD}/\text{m}^3/\text{day}$  with a COD reduction efficiency of 65% and gas production of  $0.3 \text{ m}^3/\text{kg COD}$  utilized at a  $\text{CH}_4$  concentration of 60%. The overall COD reduction efficiency of 77% was achieved during this mode of operation.

The contact methane phase enabled further enhancement of the OLR to  $5 \text{ kg COD}/\text{m}^3/\text{day}$  without adversely affecting the process performance. The COD reduction efficiency over the methane phase at an MCRT of 27 days was 70%, with an overall COD reduction of 80%. The biogas contained a higher  $\text{CH}_4$  concentration (70%). The contact mode of the operation facilitates manipulation of the MCRT, thereby enhancing process stability through greater resistance of methane formers to sulfide inhibition. These results also indicate the success of a pH control strategy to minimize sulfide inhibition in the methane phase.

The MLVSS concentrations in the methane phase have been observed to be low despite high rates of substrate utilization and gas productivity at high OLRs. This is in contrast to the concept of growth-associated methanogenesis. Mathematical models have, accordingly, been identified without the assumption of growth-associated product formation for the acid and methane phases. The models predict TVA from the acid phase within 15% of experimental values, and effluent substrate concentrations and gas yields from the methane phase within 10% and 15% of experimental values, respectively.

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#### APPENDIX II. NOTATION

The following symbols are used in this paper:

- $G$  = conversion constant to convert COD utilized to gas production;  
 $I$  = inhibitor concentration;  
 $K_i$  = sulfide-related inhibition coefficient;

- $K_s$  = substrate affinity coefficient;  
 $m$  = maintenance energy coefficient;  
 $P$  = steady state product concentration;  
 $Q$  = hydraulic flow rate;  
 $Q_{gas}$  = gas production rate;  
 $R$  = maximum rate of substrate utilization;  
 $S$  = effluent substrate concentration;  
 $S_0$  = influent substrate concentration;  
 $U_e$  = substrate utilization coefficient for energy;  
 $U_p$  = substrate utilization coefficient for synthesis;  
 $\alpha_p$  = product yield coefficient;  
 $\theta$  = hydraulic retention time; and  
 $\theta_c$  = mean cell residence time.