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ANAEROBIC DIGESTION OF HIGH SULPHATE CANE JUICE STILLAGE IN A TOWER FERMENTER

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SUMMARY

The use of a continuous tower fermenter for the anaerobic digestion of cane juice stillage, with chemical flocculant addition to accumulate biomass, is reported. While stable and efficient treatment was achieved at relatively high loading rates (>5kg COD m^{-3} day^{-1}) an operational limit was reached which restricted the maximum loading rate attainable. This was due to the composition of the cane juice stillage (predominantly high sulphate levels). Following nutrient assessment, continuous iron addition improved digester performance substantially. However, in the long term, this solution was not commercially practical due to excessive FeS precipitation which increased flocculant requirement. It is concluded that significant improvements in the loading rates achievable in this system would likely result from the digestion of (normal) low sulphur stillage.

INTRODUCTION

Despite recent interest in the use of cane juice for ethanol fermentation (Prince and Barford, 1982 b) there have been no published accounts of the anaerobic digestion of the associated stillage. However, digestion of cane and beet molasses stillages has been reported extensively (Braun and Huss, 1981, Halbert and Barnes, 1980, Roth and Lentz, 1977, Hiatt et al, 1973, Basu and Leclerc, 1972, Radhakrishnan et al, 1969, Sen and Bhaskaran, 1962). These studies have been characterised by low loadings (< 3kg BOD m^{-3} day^{-1}) at efficiencies of treatment greater than 90% with stable but high VFA levels (often > 1000 mg/l). Whilst higher loadings have been reported (5-10 kg COD m^{-3} day^{-1}) these have been associated with severely reduced treatments efficiences (less than 80%) and higher VFA levels. While cane juice and molasses stillages are for the most part similar in composition, molasses stillages contain considerably higher concentrations of inorganic salts, organic residues, and caramelized browning compounds.

We have previously reported the use of chemical flocculants in stirred flasks to assist in biomass retention and, consequently improve digester start-up performance with cheese whey and piggery effluent (Callander and Barford, 1983a, 1983b). The development of the tower fermenter, an upflow biochemical reactor utilising flocculated microorganisms has been described in detail (Callander, 1983, Prince and Barford, 1982a, 1982b, 1983c, 1983d). Initial attempts to transfer the successful flocculation work in stirred flasks to the tower fermenter was attempted with pig manure

(Callander, 1983, Callander and Barford, 1983a). While increased digester performance was achieved using the tower fermenter compared to conventional stirred digesters, it was found that the effectiveness of chemical flocculants, in the long term, was severely reduced by the high ionic strengths present (Callander and Barford, 1983c), and that the improved performance was most probably due to biomass adhesion to fibre which was retained longer. Cane juice stillage, an essentially soluble waste of lower ammonia concentration and lower ionic strength, offered the possibility of a more suitable experimental verification of the tower digester concept.

This paper evaluates the anaerobic digestion of cane juice stillage using a tower fermenter with chemical flocculant addition. Ultimately an operational limit was reached which limited the maximum loading rate attainable. This was due to the composition of the stillage rather than the effectiveness of flocculant addition or the stable operation of the tower digester (Callander and Barford, 1983c, 1983d). Further work which overcomes this limitation and achieves significantly higher loading rates will be reported shortly (Cail and Barford, 1983a, 1983b).

MATERIALS AND METHODS

The tower digester used in this work (10.7 l volume) is shown in Figure 1 and was 2.1 metres tall consisting of five 75 mm diameter QVF pipeline sections and expansion section with sidearms and a 150 mm diameter section. The full equipment description is given elsewhere (Callander, 1983).

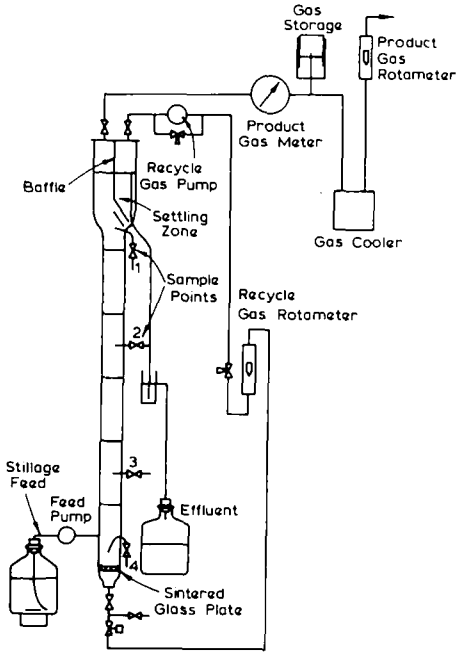

Figure 1 Tower Digester

Cane juice was supplemented with nutrients and fermented as previously described (Prince and Barford, 1982b). Fermentation beer was distilled to remove ethanol and frozen until use in 20 l drums. Distillation and subsequent dilution with water were carried out to give an overall concen-

tration factor from "beer" to stillage of 1.22, corresponding to current industrial practice. During dilution, an additional nutrient (iron) was added and the stillage pH adjusted to 4.5 - 5.0 with sodium hydroxide to maintain a digester pH of 7.2 - 7.4. The cane juice stillage had the following composition (mg/l): COD, 26,000; TS, 23,700; VS, 16,900; TSS 2,030; VSS, 1,880; Ethanol, 1,980; Glucose and Fructose, 3,860; Sucrose, 310; Glycerol, 4,740; Total Nitrogen, 1,190; Ammonia Nitrogen, 940; Total Phosphorus, 320 (soluble, 296) Orthophosphate, 228; Sulphate, 1,470; Sulphide (soluble < 5); Sodium, 510 (soluble, 540); Potassium, 2,100 (soluble, 2,000); Magnesium, 238 (soluble, 220); Calcium, 210 (soluble, 206); Iron, unsupplemented, 15 (soluble, 5), supplemented, 615 (soluble, 500); Cobalt, 0.6 (soluble, 0.2); Nickel, 1.0 (soluble, 0.3); Copper, 125 (soluble, 50); Zinc, 35 (soluble, 33); pH, 3.91. Because of nutrient additions in ther fermentation experiments, the stillage contained abnormally high sulphate levels. While commercial sugar cane stillages would not contain such a high sulphate level, this work does serve to demonstrate the consequence of adding H_2SO_4 for pH adjustment during ethanol fermentation or nutrients as sulphate salts.

Seed sludge was obtained from a cane juice stillage pilot scale ($2m^3$) digester at the Sugar Research Institute, Mackay, Queensland. A wide range of commercially available synthetic organic flocculating agents had been tested for flocculant effectiveness and toxicity in the piggery manure digestion work (Callander and Barford, 1983a, c; Callander, 1983). The two most effective flocculants, Zetag 76 and Zetag 88N (Allied Colloids) were used in this work (Zetag 76 until day 203). Flocculant addition commenced on day 81.

The following measurements were made routinely: pH, alkalinity, total and volatile solids, total suspended solids and volatile suspended solids, volatile fatty acids, gas analyses (CH_4, CO_2, H_2S, N_2, O_2, H_2), total nitrogen, ammonia nitrogen, total phosphorous, orthophosphate, COD, soluble sulphide, soluble sulphate, metal analysis (K, Na, Ca, Mg, Fe, Co, Ni, Cu and Zn).

RESULTS AND DISCUSSION

The performance of the tower digester with cane juice stillage is shown in Figure 2. The feed loading commenced at 0.8 kg COD m^{-3} day^{-1} amd was increased in steps to 1.35 kg COD m^{-3} day^{-1} to day 127. During this period soluble COD reduction was 93-96% (Total COD 92.5 - 95%) with gas composition averaging 64% CH_4, 32.8% CO_2 and 0.6% N_2. Volatile fatty acid levels of less than 100 mg/l acetic acid and less than 20 mg/l propionic acid indicate process stability. A mass balance indicated approximately 9% COD feed converted to biomass. The effectiveness of flocculant addition in assisting the accumulation of biomass within the digester is illustrated by a comparison of biomass accumulation before and after flocculant addition. Before flocculant addition (day 62) biomass concentrations increased from 4.8 to 5.5 gVSS/l compared to an increase to 11.3 gVSS/l at day 132 (effluent biomass concentration 0.4 - 0.5 gVSS/l) following flocculant addition. Further increases in biomass accumulation were observed over the duration of the experiment - 12.3 gVSS/l, day 205; 17.3 gVSS/l, day 240; 26.0 gVSS/l day 323.

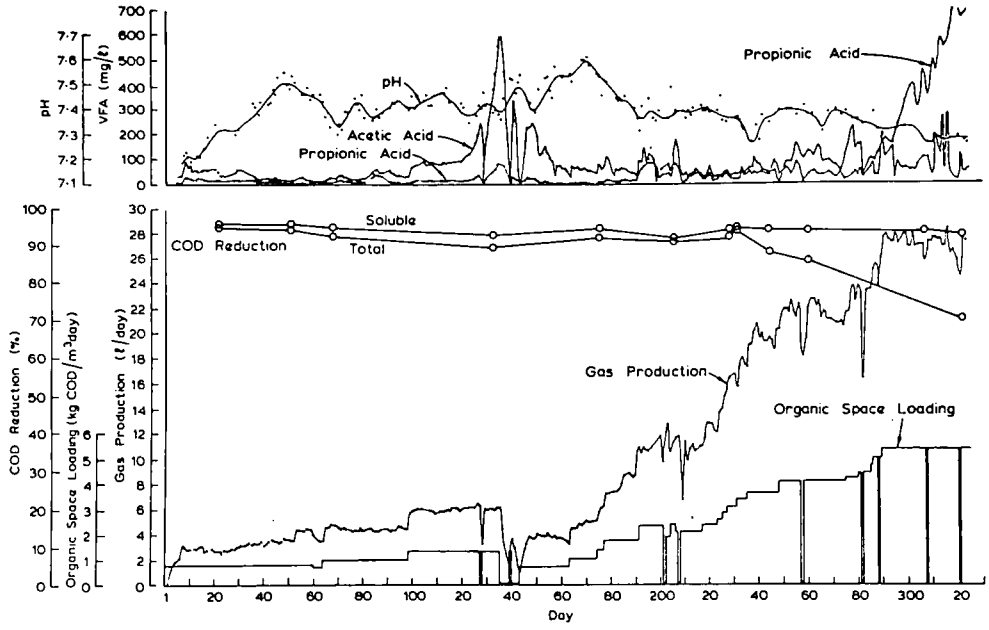

Figure 2 Performance of Tower Digester with Cane Juice Stillage

Between day 127 and 142, the digester process became unstable and feeding was stopped three times to allow VFA levels to fall. This period was characterised by rising VFA levels. While feed stoppage allowed the digester to recover, it was not a permanent solution since no further increase in loading rate was possible. It was clear that any increased loading from this point would almost certainly lead to digester failure unless the cause of this instability was determined and rectified. At the high sulphide levels present in this work, such a process failure would have probably been attributed to sulphide inhibition (Lawrence et al, 1964).

An assessment of nutrient availability in anaerobic digestion (Callander and Barford, 1983d, e) suggested that iron availability is also severely reduced in the presence of sulphides. A sulphur mass balance on feed, tower contents, effluent and product gas indicated that 21% of the available sulphur was possibly removing iron from its nutritionally available form (Feed sulphur 100%, gas (H_2S) sulphur 45%, effluent sulphur - H_2S and HS^-, 29%; SO_4^{2-} 5%). Whilst these results suggested that soluble iron addition to the tower digester would probably increase digester activity, it should be noted that the assessment of nutrient availability in anaerobic digesters is complicated by the vast range of compounds normally present and the lack of routine analytical procedures to determine biological availability.

From day 143 continuous iron addition was undertaken and the space loading was restarted at 0.8 kg COD m^{-3} day^{-1}. This resulted in a steady reduction in VFA levels at this feed loading to 32 mg/l acetic and 2 mg/l propionic acid by day 163. The level of soluble iron remaining was 0.5 mg/l compared to less than 0.2 mg/l before supplementation. As a consequence of this

measure, feed loading was increased in steps from 0.8 to 5.3 kg COD m^{-3} day^{-1}. Stillage conversion during this period ranged from 92.3 to 95% based on soluble COD (86-94% based on total COD). Gas methane content varied from 62% at loadings of 0.8 - 1.0 kg COD m^{-3} day^{-1} to 58% at 5.3 kg COD m^{-3} day^{-1}. Up to a loading of 4.1 kg COD m^{-3} day^{-1}, VFA levels remained low at 50 mg/l acetic and < 100mg/l propionic acid.

Iron addition, however, despite giving a markedly increased digester performance, was not considered to be a feasible long term solution to the digestion of cane juice stillage. From day 57 to day 323, the inorganic suspended solids accumulated in the tower digester from 2.5 g/l to 54.6 g/l. This twenty-fold increase in inorganic solids level indicates a preferential retention of heavy iron sulphide compared to biomass, which only increased by a factor of 5.5 in the same period. Not only did this precipitate occupy a considerable proportion of the tower volume, but it also would have accounted for much of the increased flocculant addition during the last 100 days of the study. Loadings in excess of 5.3 kg COD m^{-3} day^{-1} were not possible. These loadings, nonetheless, compare favourably with previously reported loadings on molasses dunders. A significant improvement would be expected with a low sulphur cane juice stillage where these problems would not be present. A considerable control over sulphate levels in stillage may be exerted during the processing and fermentation of sugar cane.

CONCLUSIONS

A continuous tower digester, employing flocculant addition to accumulate high biomass density, is able to stably digest cane juice stillage rapidly and efficiently. The performance reported in this study was probably limited by high soluble sulphide, FeS precipitation following iron supplementation to overcome digestion instability and consequent high flocculant requirement. Significantly improved performances would be expected from (normal) low sulphur stillage.

ACKNOWLEDGEMENT

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