Application of Acidogenic Solids Removal in the Biological Treatment of Wastewater from a Bagasse Based Pulp and Paper Mill.

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1. Introduction

Integrated pulp and paper mills produce two wastewater streams (Smook, 1993). The first and most polluted, called black liquor is drained from the pulp directly after the pulp digestion process. This stream contains the cooking chemicals and the organics (primarily lignin) extracted from the fibre during cooking. Usually black liquor is incinerated to recover the cooking chemicals and generate steam used in the mill.

The second wastewater stream (or mill wastewater) is a mixture of all other waste streams from the mill. This stream consists primarily of excess water from the paper making process, called backwater, but it will also contain water from pulp plant drains and any ancillary processes. In most cases, this water can be treated using conventional primary, secondary and tertiary wastewater treatment systems before being reused in the mill or disposed of into the environment.

The mill for which this work was done currently discharges both of these streams to sea. This is becoming an increasingly undesirable practice due to ever increasing environmental legislation (Water Act of 1998), and public pressure. Ideally, the mill would aspire to "Zero Liquid Effluent" (ZLE) status as advocated by Webb (1997). However, this would require treatment of both the black liquor and the mill wastewater stream.

Since the mill is small, incineration of the black liquor is not financially viable though the possibility exists to add it to the black liquor of another mill in the area for incineration and chemical recovery. Since the stream would be incinerated, it would not no longer contribute to the total liquid effluent.

The remaining challenge faced by the mill, and the subject of this work, is to treat the mill wastewater stream for reuse in the mill. Reuse of the treated wastewater would reduce the quantity of fresh water intake, and eliminate the need to discharge this wastewater stream. Of primary concern are the removal of total suspended solids (TSS) and chemical oxygen demand (COD).

The wastewater stream to be treated consists primarily of backwater, and excess water from the bagasse handling system, referred to as reclamation water (Botes, 1981). Both streams have high TSS and COD levels resulting in a mixed stream with average TSS and COD levels averaging approximately 2400 $mg.l^{-1}$ and 11500 $mg.l^{-1}$ respectively.

TSS levels need to be reduced to 50 mg.l^{-1} for use in spray applications where nozzle suppliers list nozzle fouling as a concern. Higher TSS levels are acceptable in dilution and pulp washing applications where nozzles are not used. However, according to Webb (1997) even in these applications the TSS levels need to be as low as possible to reduce build-up of high cationic demands in the pulp that interfere with and consume "wet end" chemical additives added to the pulp before it goes to the paper machine. Barascud *et al.*, (1989) emphasise that COD removal is required to reduce biological slime build up commonly found in paper mills with closed water systems (Hunt & Pretorius, 1999).

Laboratory investigations showed that conventional treatment methods were not feasible as the high TSS levels resulted in high coagulant cost with chemical treatment, or a build-up of inert mixed liquor suspended solids (MLSS) fractions, and therefore poor sludge performance, in conventional anaerobic and aerobic treatment systems.

The findings of preliminary investigations, and concepts taken from the literature (Zeeman *et al.*, 1997 and Liu & Ghosh, 1997), suggested that a two stage anaerobic system could be used. In the first (acidogenic) stage the pH is lowered to enhance flocculation and remove the bulk of the TSS, while in the second (methanogenic) stage the soluble COD is biologically removed. Further treatment using aerobic treatment to improve wastewater quality was also indicated (Priest, 1980).

This study describes various experiments conducted to determine the feasibility of using an acidogenic solids removal stage, and whether the resulting effluent could be treated using a conventional anaerobic-aerobic series treatment system. The work was aimed at producing a final effluent of sufficiently high quality that it could be reused in the mill for spray, pulp washing and dilution applications.

2. Literature Review

2.1 Origins of Pulp and Paper Mill Wastewater

The general layout and operation of pulp and paper mills, as described below, is very similar in most cases. Smook (1994) gives a comprehensive overview of the pulp and paper industry from which the following description is derived.

A generalised block diagram of and integrated Pulp and Paper Mill is given in Figure 1 showing the origins and handling of the wastewater streams.

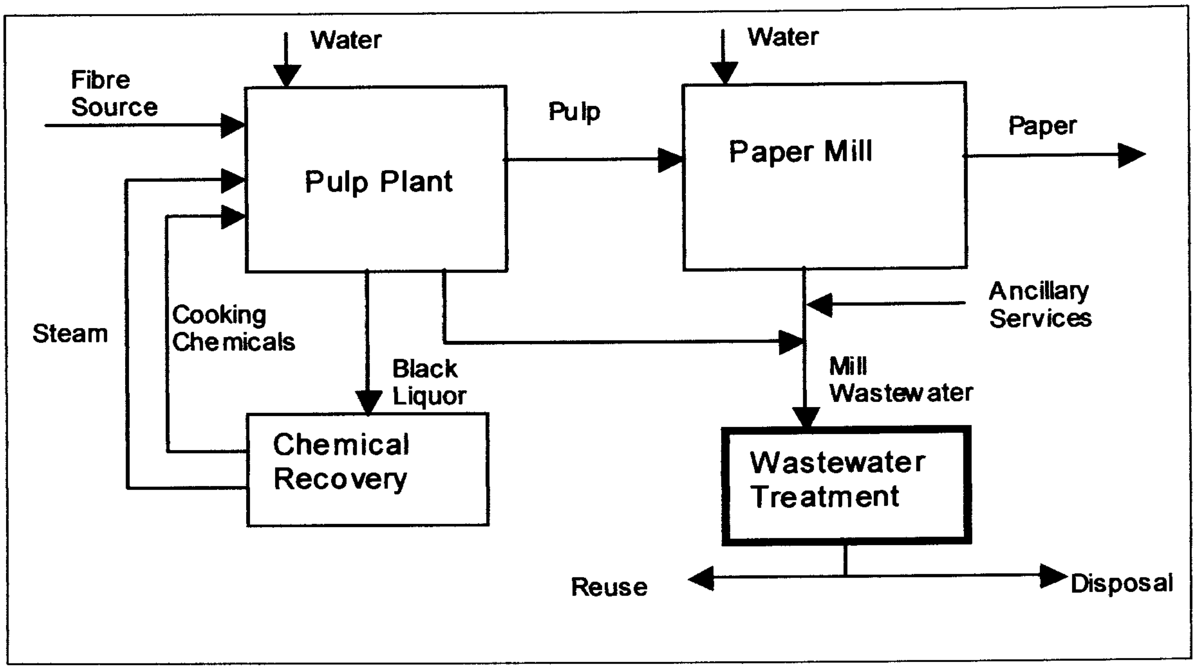

Figure 1: Generalised flow diagram for integrated pulp and paper mills.

2.1.1. Black liquor

Black liquor is produced during the pulp cooking process and contains residual cooking liquor, fine suspended organic and inorganic material, and dissolved lignin and extractives released from the fibre source during cooking. It therefore has high COD, colour, sodium and TSS concentrations. Most of the black liquor is removed from the pulp during pulp washing operations and is treated separately to the mill effluent. In most large mills, the black liquor is incinerated to recover the cooking chemicals and to generate steam for the process. Because of the high capital cost of chemical recovery systems, they are often not viable for smaller mills and the black liquor is disposed of into the environment. This is the case with the mill in question disposes of its entire wastewater stream through a marine outfall pipeline that serves industries in the area.

2.1.2. Mill Wastewater

Sources

1. Backwater - When pulp reaches the paper machine, it is diluted with "white water" which carries it onto the paper machine. Residual black liquor in the pulp is diluted into the white water. The white water, which is continuously recirculated from the paper machine back to the pulp dilution stage, is therefore contaminated with residual COD, TSS, sodium and colour contained in the pulp coming from the pulp mill. Since the moisture content of pulp entering the system is higher than that of the paper leaving the system, there is always excess white water. The excess white water overflowing from the paper machine system is referred to as backwater and is collected in the backwater tank for use in the pulp plant for dilution. Surplus backwater overflows to the wastewater system.

2. Mill drains - Drains in both the pulp and paper mill are used to collect various wastewater sources such as washdown water, spills and glandservice water. These drains combine with the mill wastewater.

3. Ancillary sources - All mills have ancillary services such as raw materials handling, power plants and chemical plants from which wastewater streams are discharged into the mill wastewater systems.

Wastewater Treatment

Since pulp and paper mills usually fit into the generalised model described above they face the same challenges with respect to wastewater treatment. Pulp and paper mill wastewater is generally treated using conventional primary settling, secondary biological treatment and, if required, tertiary advanced treatment methods (Dorica, Ramumurthy & Elliot 1999). Depending on the situation the water is reused as far as possible while excess water is disposed of into the environment (Webb, 1997). The treatment options discussed below have been used in the industry, and were taken into consideration when investigating treatment of wastewater from the mill in question.

2.2 Chemical treatment

As the coarse suspended solids in mill wastewater tend to settle well, and fine suspended solids are removed in secondary treatment systems, coagulation and flocculation are seldom used in the pulp and paper industry to enhance primary settling (Springer, 1993). However, coagulants and flocculants have been used in:

- Internal recycle loop clarification of cleaner streams (Webb, 1997);
- Solids flotation units where strong floc formation is essential (Springer, 1993);
- Enhancement of activated sludge treatment (Volpe *et al.*, 1998); and
- Tertiary treatment to clarify activated sludge effluent (Jansen *et al.*, 1998).

In all cases where chemical coagulation was reported, the streams to be cleaned were from mills that bleached their pulp indicating that the pulp is washed to remove 99% of the "washable" black liquor solids (Smook, 1994; 101). The use of coagulants and flocculants are not recommended for the treatment of wastewater from the mill in question as the pulp washing stage only removes approximately 40% of "washable" black liquor solids.

Ross (1982) found that when acid was used to lower the backwater pH to 4, lignin precipitated, entrapping other fine suspended solids in the wastewater, effectively flocculating most of the TSS. However, the sludge formed in this way does not dewater easily. Furthermore, Webb (1997) found that addition of inorganic acids was undesirable, if the water was to be reused, as the pH had to be neutralised by addition of a base, thus adding to costs, and to total dissolved solids content that can cause equipment corrosion and scaling in paper mills.

From the above it is clear that chemical precipitation, using either conventional coagulants or acid mediated precipitation is not an acceptable solution for treating the mill wastewater and will therefore not be dealt with further.

2.3 Biological Treatment

2.3.1. Biological TSS and COD Removal

Biological treatment configurations including anaerobic systems, aerobic systems and anaerobic-aerobic series systems have been widely implemented in the paper industry (Qui, Fergusson & Benjamin, 1987). The primary focus in biological treatment research has historically been on activated sludge systems, but Lee, Patterson & Stickney (1989) suggest that developments in anaerobic treatment technology have resulted in its acceptance in the industry. The advantageous use of combined anaerobic/aerobic series systems (Qui *et al.*, 1987) is also becoming well recognised within the pulp and paper industry and elsewhere.

Most mills dispose of excess treated wastewater by discharge into local water bodies, making TSS removal important to reduce sediment formation, while COD removal is important as disposal of COD rich wastewaters causes oxygen depletion in the receiving water (Springer, 1993).

Apart from returning wastewater to the environment, recovery of wastewater for reuse by pulp and paper mills is becoming common practice (Webb, 1997). Commonly referred to as "closing the loop", reuse of water is pursued to reduce fresh water consumption and wastewater discharges in response to pressure to reduce environmental impact. Ogden & Wiseman (1997) and Webb (1997) found that the paper industry is fortunate that most of its wastewater streams are amenable to biological treatments that are usually used to reduce TSS and COD levels.

TSS levels need to be controlled in wastewater to be reused in paper mills as the fine particulates found in waste streams tend to foul spray nozzles and cause increased chemical dosing requirements on the paper machine (Webb, 1997). Usually the TSS can be removed by chemical flocculation followed by solids separation (Volpe *et al.*, 1998). Springer (1993) discussed the use of activated sludge systems in removing TSS by incorporation of the solids into the sludge. However, this causes an increase in the inert fraction of the sludge if the TSS levels are too high or the sludge retention time too long.

Barascud *et al.*, (1992) showed the importance of removing COD from water to be reused within pulp and paper mills, where accumulation of high COD levels in closed systems results in slime build up in water reticulation systems leading to equipment corrosion and paper quality problems.

Since the nature of pulp and paper wastewater lends itself to biological treatment systems for the reduction of both TSS and COD the possibility of using some form of biological treatment should be considered whether the water is to be discharged into the environment or reused by the mill. An understanding of the application and potential of anaerobic and aerobic biological treatment systems is essential in determining the best options for mill wastewater streams. The general applications, and pulp and paper mill specific applications, of various biological treatment concepts are discussed below.

2.4 Anaerobic Treatment

The treatment system proposed in this work involves the use of a two stage anaerobic system in which the first (or acidogenic) stage acts as a solids removal step before further treatment of the wastewater in the second (or methanogenic) stage. To develop an understanding of these processes and there application to the pulp and paper industry the following review will describe the overall anaerobic process, application of anaerobic treatment in the pulp and paper industry, two stage anaerobic systems and the application of the acidogenic stage for solids removal.

2.4.1. The anaerobic process

In anaerobic treatment processes, a consortium of facultative and anaerobic organisms, is used to treat wastewaters (McKinney, 1983). As described by Lee *et al.* (1989) complex organic compounds are sequentially stabilised and converted to methane and carbon dioxide in a series of fermentation reactions as listed in Table 1. In two stage anaerobic processes, which are discussed in more detail later, these processes are broadly grouped into the acidogenic and methanogenic stages (Alexiou *et al.*, 1994)

Table 1: Anaerobic processes and bacteria, and two-stage subdivision (Lee et al.*, 1989 and Alexiou* et al.*, 1994).*

Process	**Activity**	**Bacteria type**	**Two Stage system stages.**
Hydrolysis	Complex organic compounds are hydrolysed to simple compounds such as simple sugars.	Hydrolytic bacteria	Acidogenic (VFA production)
Fermentation	Simple compounds are converted to higher organic acids, acetic acid, hydrogen and carbon dioxide.	Acid forming (acidogenic) bacteria	
Acetogenesis	Conversion of higher organic acids to acetic acid and hydrogen.	Acetigenic bacteria	Methanogenic (VFA conversion)
Methanogenesis	Conversion of acetic acid, formic acid, methanol, carbon dioxide and hydrogen to methane.	Methanogenic bacteria	

Anaerobic treatment configurations

A number of anaerobic treatment configurations have been developed. Those reported by Lee *et al.* (1989) to have found application in the pulp and paper industry include: anaerobic lagoons; anaerobic contact reactors; upflow anaerobic sludge bed reactors (UASB); anaerobic filters; and anaerobic fluidised bed reactors. Hybrid combinations of the above have also been used. Of the above, the UASB seems to have found the greatest acceptance due to its high reaction rate. The pelletised sludges formed in UASB reactors make biomass retention relatively simple without incurring the cost of packing materials used in fixed growth systems. However, high TSS levels inhibit all the high rate systems either by accumulation of inert material in the sludge or by causing blockages in fixed medium systems. Lettinga & Hulshoff Pol (1991) recommended for UASB reactors that the TSS should be less than 10% of the COD concentration. It is thus important that the TSS of paper mill wastewater should be reduced as far as possible if the use of a UASB process is considered.

2.4.2. Anaerobic treatment in the pulp and paper industry

Mechanical and chemical pulping of wood and other raw materials used in the pulp and paper industry results in the release of soluble extractives. As reported by Lee *et al.* (1989), some of these, such as lignin derivatives, are refractory to biodegradation while others, such as carbohydrates and some organic acids, are easily degraded under anaerobic conditions.

Priest (1980) describes the treatment of the entire waste stream from a waste paper based mill, while Valesco, Bonkoski & Samer (1986) discuss the treatment of the entire wastewater stream from a mill using straw and wood, digested with sodium hydroxide, and waste paper in an anaerobic contact reactor systems. These studies are significant in that the wastewaters treated are similar to the type of wastewater to be treated in this study.

Hall & Comacchio (1988) screened 42 in-plant waste streams from 21 Canadian pulp and paper mills to assess their potential amenability to anaerobic treatment. The screening process used chemical characterisation (COD, BOD, VSS, and sulphates) and an anaerobic serum bottle technique to demonstrate biodegradability. Of the various effluent streams from kraft, sulphites, mechanical, and semichemical mills, 23 (55%) were found to be suitable for anaerobic treatment. After microbial adaptation and/or removal of inhibitory factors, other process streams also became amenable to anaerobic treatment. For example, residual peroxide in peroxide bleaching effluents is toxic to methanogens but is readily eliminated by acidogenic treatment.

Further benefits of acidogenic treatment were shown by Barascud *et al.* (1992) who demonstrated that a two stage anaerobic process was effective in maintaining low TSS and COD levels in a simulated paper mill water circuit. The acidification stage was found to attenuate changes in wastewater composition by converting sugars to VFAs and hydrolysing larger compounds such as starch. This resulted in a more constant feed to the anaerobic second stage, making it possible to maintain its efficiency.

COD loading rates for anaerobic treatment plants used in the pulp and paper industry are as given in Table 2.

Table 2: Anearobic COD loading rates from literature.

Measure of COD loading rate	UASB reactors in Pulp and Paper industry
mg COD/mg MLSS/d	7 to 10
kg COD.m-3.d-1	6 to 24
Reference	Lee *et al.* 1989

The above references show that anaerobic treatment, and two stage anaerobic systems, are valid technologies in the pulp and paper industry and should always be taken into consideration when designing mill wastewater treatment systems. Specific considerations as they pertain to the pulp and paper industry are discussed below.

Nutrient requirements

Because anaerobic processes have lower biomass yield than aerobic processes, they generally need one-third or less of the nutrients required by aerobic systems. For anaerobic biomass, the nitrogen requirement is approximately 11 %, while phosphorus is approximately 2% of the net biomass yield (Lee *et al.*, 1989). Qiu *et al.* (1987) adjusted the influent COD:nitrogen:phosphorus ratio to 100:1.2:0.1 and achieved good results in their bench scale UASB reactor, illustrating the low nutrient requirement of anaerobic systems relative to aerobic systems in which the ratio is in the order of 100:2.5:0.5 (Springer, 1993). This is important to the pulp and paper industry as mill wastewaters usually have low phosphorus and nitrogen concentrations (Lee *et al*, 1989).

McKinney (1983) showed that a major breakthrough in the development of anaerobic systems was the discovery of iron, cobalt, nickel and molybdenum in the enzyme systems of methanogenic bacteria. Supplying these trace elements to anaerobic systems has been found to treble reaction rates in some cases, and to improve the stability of anaerobic systems making them more acceptable for pulp and paper wastewater treatment. In their investigation Lee *et al.* (1989) found that all required micronutrients (1-5 ppm iron and nickel, and 0.05 ppm cobalt, molybdenum, and selenium) are usually present in the wastewater due to equipment corrosion in the pulping process.

The above indicated that bio-available sources of nitrogen (N) and phosphorus (P) would possibly be required but trace elements would not be required in the proposed treatment process.

pH and Alkalinity

McKinney (1983) reported the optimum pH in single stage anaerobic treatment systems to be between 6.5 and 7.5. This range suits the methanogenic organisms which are rate limiting. Methanogenic activity slows down below 6.5 to almost total suspension at 6.0. Good results can be obtained at pH as high as 8.5 but they will not be as good as at 7.5. McKinney suggested that limitation at high pH is due to precipitation of essential trace metals. In anaerobic systems, pH tends to drop due to CO_2 and VFA formation and alkalinity of 1000 - 5000 $mg.l^{-1}$ as $CaCO_3$ is required to maintain acceptable pH levels. Usually this is added as required in the form of sodium bicarbonate, lime or sodium hydroxide.

The mill wastewater to be treated has an alkalinity of between 1200 and 2000 $mg.l^{-1}$ and a pH of between 4.8 and 6.1 due to VFAs in the reclamation water. Since the proposed system involves pre-acidification, the pH of the water entering the methanogenic stage is low averaging 5.14. The method used to overcome this problem is discussed later.

Inhibition and Toxicity

According to Lee et al. (1989) anaerobic and aerobic bacteria are usually equally affected by toxins and inhibitory compounds but anaerobes are better able to acclimatise to unfavourable environments. However, due to the relatively low growth rate of methanogens toxic effects in the anaerobic digester are usually more long lasting. The inhibitory or toxic compounds and conditions reported by Lee *et al.* (1989) & McKinney (1983) to be of potential concern in anaerobic treatment of pulp and paper process wastewaters include:

- Inorganic sulphur compounds (sulphate, sulphite, and sulphide) from cooking liquors.
- Oxidants, such as chlorine and peroxide, used for pulp bleaching.
- Volatile organic acids and wood extractives, including resin acids, produced during pulp digestion.
- Heavy metals from machine wear.
- Organic additives such as defoamers, biocides and cleaning agents.

Many of these can be ameliorated using a pre-acidification stage as discussed earlier. Because the acidogens are hardy and facultative, they eliminate oxidising agents and are more able to hydrolyse complex toxic organics under the favourable conditions in which they are maintained in an acidogenic reactor (Alexiou *et al.*, 1994).

2.4.3. Two stage systems

In two stage anaerobic systems the VFA forming bacteria (acidogenic bacteria) are separated from the VFA converting bacteria (methanogenic bacteria) in two separate stages referred to as the acidogenic (or pre-acidification) stage and the methanogenic stage. This is possible because the acidogenic and methanogenic bacteria differ in terms of optimum environmental conditions and metabolic rate as follows:

1) pH range – Although no upper limit was indicated in the literature Speece (1997:94) recorded one instance of an acidogenic reactor, treating starch plant effluent, operating at pH 3.6. Romli, Greenfield & Lee (1993) reported the pH range for methanogens to be between 6.5 and 8.
2) Optimum pH - Zoetmayer *et al.* (1982) recorded an optimum acidogenic pH range of between 5.8 and 6.2 while Romli *et al.* (1993) showed that the optimum pH for methanogens was between 7 and 7.2.
3) Metablic type - Acidogens are facultative, and are therefore able to tolerate oxygen, while methanogens are strictly anaerobic and find oxygen and other oxidising agent toxic (Liu & Ghosh 1997).
4) Metabolic rate - Acidogens tend to have higher metabolic rates and are generally hardier than methanogens (Liu & Ghosh 1997).

In single stage anaerobic systems, the two groups are maintained under conditions favouring the methanogens by restricting the nutrient supply to the reactor (Liu *et al.*, 1997). In this way the metabolic rate of the acidogens is restricted such that the methanogens are able to metabolise the VFAs at the rate they are formed thereby maintaining the reactor pH within the methanogenic range (Zeeman *et al.*, 1997). The presence of a sufficient concentration of alkalinity (usually greater than 1000 mg.l^{-1}) is critical in helping to buffer the pH against system fluctuations (Nishimura & Yoda, 1996).

In two stage systems two reactors are used in which the first is made acidogenic by running it with a feed nutrient supply rate such that the VFA production exceeds the rate at which the methanogens are able to metabolise the VFAs. Under these conditions, the pH drops to below the minimum methanogenic pH tolerance level of 6.5 and the methanogens are selected out of the reactor (Zeeman *et al.*, 1997). The acidogenic reactor effluent then goes to the second reactor in which conditions are optimised for methanogens and the VFAs are metabolised into methane. Lettinga & Hulshof Pol (1991) and Moosbrugger *et al.* (1993) found that complete acidification of all available substrates is not desirable in acidogenic reactors preceding UASB methanogenic reactors as the hydrogen produced in the acidogenic reactions seems to be required for the pelletised sludge formation critical to UASB reactors.

In the treatment of paper mill effluent, it might be necessary to supplement the wastewater with a source of biodegradable organic substance to enhance acid generation in the acidogenic stage, and hydrogen generation in the methanogenic stage if a UASB reactor is used.

2.4.4. Advantages and application of two stage anaerobic systems

Two-stage anaerobic systems are advantageous because they enable optimisation of the separate stages by controlling the two reactors at conditions best suited to each group of bacteria (Nishimura & Yoda, 1996). Because acidogens are facultative and hardier than methanogens, the acidogenic stage can also be fed with wastewater containing oxidising agents (such as oxygen and peroxide) and other substances that can be metabolised by acidogens, but are toxic to methanogens (Lee *et al.*, 1989). The acidogenic stage then protects the methanogenic stage by metabolising these toxins before the wastewater reaches the methanogens. Zeeman *et al.* (1997) showed that the acidogenic stage could be used, when followed by a settling stage, for solids removal in some application. This concept and its application to the mill wastewater treatment concept proposed here is discussed in more detail later.

A problem with using two stage systems is that the low pH of the acidogenic effluent is not suitable for the methanogenic stage. Nishimura & Yoda (1996) and Romli et al. (1993) overcame this by recirculating a portion of the methanogenic effluent to mix with the feed coming from the acidogenic reactor thereby increasing the pH to within the methanogenic pH range.

2.4.5. Application of acidogenic solids removal

For wastewaters with COD levels in excess of 10 $g.l^{-1}$ an acidogenic stage followed by solids separation was found by Lettinga & Hulshoff Pol (1991) to be beneficial for preparing high strength wastewaters for treatment in UASB reactors. This is because the solids, including biomass, produced in the acidogenic stage reactor, which tend to interfere with UASB sludges are removed in the settler.

Zeeman *et al.* (1997) used an upflow anaerobic solids removal reactor (UASR), modelled on the UASB reactor configuration, to remove solids from dairy wastewaters and sewage. In dairy wastewaters casein precipitates, encapsulating lipids, below its isoelectric point at pH 4.6. In the UASR reactor, acidogens converted sugars, such as lactose, to VFAs dropping the pH to below 4.6. It was therefore possible to remove most of the solids in the wastewater in the acidogenic reactor. Similar results were also reported for sewage sludge.

Acidogenic feed rates quoted in the literature include 28 kg COD.m^{-3}.d^{-1} for starch plant wastewater given by Speece (1997: 94). From their work on acidogenic solids removal using an UASR reactor, Zeeman *et al.* (1997) give the performance data in Table 3 for the three trials they ran. No record could be found for optimum loading rates for solids removal applications.

Table 3: Solids removal performance of UASR reactor.

COD Load kg COD.m^{-3}.d^{-1}	HRT h	Temp °C	Removal %	Wastewater type
5.6	3	17	65	Raw sewage
4.5	9.6	20	98	Waste activated sludge
21.2	4.5	20	98	Dairy wastewater

In theory it was considered possible to reduce the pH of the wastewater in question to less than 4 inducing lignin precipitation. After settling out the flocs formed the supernatant would then be suitable for methanogenic stage treatment. As reported later it was found in practice that biological floc formation occurred below pH 5.5.

2.5 VFA production from molasses

The use of molasses as a substrate for VFA production requires an estimate of the VFA production capacity of molasses in order to determine the quantity of molasses required. As calculated in Appendix 1, 1g of molasses will yield 0.439g of acetic acid.

2.6 Aerobic Treatment

Aerobic treatment often finds greater acceptance in the pulp and paper industry as it has been in use longer, and more widely, than anaerobic systems. Storage oxidation basins, aerated stabilisation basins and activated sludge systems have been used with activated sludge being the most widely used (Springer, 1993). The technology is well understood and effective but it has its limitations and disadvantages. For example, the quantity of sludge produced and energy consumed are higher in aerobic systems than in anaerobic systems (Lee *et al.*, 1989).

According to Webb (1997), sequencing batch reactor (SBR) activated sludge systems have found favour in recent years and are being used in a number of Canadian mills. The advantages given for SBR systems include:

1) greater flexibility;
2) better settling under ideal quiescent conditions;
3) high COD concentrations during the early stages which selects against filamentous bacteria;
4) good dilution of slug concentrations due to complete mixing;
5) lower operating and capital costs; and
6) the option to allow anaerobic conditions to develop is also available which is useful in inhibiting sludge bulking filamentous organisms.

COD loading rates for activated sludge in the pulp and paper industry are as given in Table 4.

Table 4: Aerobic COD loading rates from literature.

Measure of COD loading rate	Activated sludge reactors in Pulp and Paper industry
kg COD/kg MLSS/d	0.4 to 1
kg COD.m-3.d-1	> 3.2
Reference	Springer, 1993

Because of the above, and for practical convenience, an SBR activated sludge system was ideally suited for laboratory work.

2.7 **Anaerobic/aerobic**

Use of the anaerobic systems has been found to be beneficial in reducing the COD load on subsequent aerobic systems by either treating the whole stream (Qui *et al.*, 1987), or just the most concentrated contributing streams (Driesen & Wasenius, 1994). In the anaerobic treatment stage, full anaerobic systems (Anderson *et al.*, 1985) and pre-acidification systems (Eroglu *et al.*, 1994 and Priest, 1980) have been used. Anderson *et al.* (1985) also showed that anaerobic processes could be effectively used to select for floc forming organisms in subsequent activated sludge systems thereby improving aerobic treatment performance. Due to the decreased load on the aerobic system addition of an anaerobic pre treatment has been used to increase the capacity of existing aerobic systems at lower capital and operating cost than would have been incurred by increasing the aerobic system capacity (Eroglu *et al.*, 1994 and Priest, 1980).

However, aerobic final treatment is required to reduce biochemical oxygen demand (BOD_5) to acceptable limits, increase dissolved oxygen (DO) and oxidise reduced odorous substances such as hydrogen sulphide (Qui *et al.*, 1987).

These findings show that biological treatment systems can be optimised in terms of reactor volume requirement and capital cost, operational cost, sludge volume production and final effluent quality by using anaerobic and aerobic treatment systems in series.

2.8 Research Objectives

The main objectives of this study was to evaluate a biological wastewater treatment system that will reduce the TSS and COD of the mills effluent (a mixture of backwater and reclamation water) to such a quality that it could be reused within the mill or would improve the mills current compliance with wastewater discharge requirements.

For practical purposes the research has been conducted in two phases:

1. Acidogenic batch reactor studies to determine the effect of wastewater composition, and addition of nutrients, on the solid removal by acidogenic treatment and settling.
2. Application of the results from the batch reactor studies to an acidogenic CSTR reactor followed in series by settling, methanogenic treatment, and aerobic (activated sludge) treatment.

From the results obtained, preliminary design criteria for full-scale application of the above treatment regime were derived.

3. Experimental

3.1 Wastewater origins and characteristics

The mill in question is a bagasse and wastepaper based fluting mill. This has two important implications: firstly, the pulp is not well washed, as it is not critical to fluting manufacture; and secondly there is a source of reclamation water, which is specific to bagasse mills. As mentioned above, the wastewater stream treated was made up primarily of backwater and reclamation water. The origins of these streams and the properties of the combined stream are discussed below.

Backwater

Lignin is removed chemically from pulp by cooking it at high temperature and pH. In the case of this mill, the bagasse is cooked under pressure at a temperature of 170°C using 135kg of sodium hydroxide, added as a 125g.l^{-1} aqueous solution, per ton of bagasse. A final pH of approximately 10 is reached. Under these conditions, the lignin is soluble so that it is removed by draining the black liquor from the pulp during pulp washing. Because the pulp in this mill is not well washed, residual lignin is carried forward in the pulp to the paper machine and ends up in the backwater system. The backwater has a pH of between 8 and 9.5 and a TSS of between 3000 and 5000 mg.l^{-1}.

Reclamation water

An acidic culture (pH 4), called Ritter water is used to hydraulically convey milled bagasse, from the sugar mill, onto a stockpile. A residual quantity of Ritter water remains in the stockpile, while it is being compacted, which is sufficient to maintain the low pH required to inhibit biological degradation of the bagasse (Botes, 1981). Ritter water is generated using a fermenting mixture of molasses and water with sour milk used as an inoculum. The Ritter water culture is sustained through metabolism of residual sugars in the bagasse (Botes, 1981).

Bagasse is recovered from the stockpile and transported to the bagasse washing plant by hydraulically conveying it using reclamation water. During bagasse reclamation, residual Ritter water is incorporated into the reclamation water stream resulting in excess that overflows to the mill wastewater system. The accumulation of Ritter water in the reclamation water gives it a low pH (4 to 4.5) and an acidogenic bacteria population.

Combined flow

Approximately 800 kl of excess reclamation water and 1600 kl (i.e. 1:2 mixture) of excess backwater mix in the wastewater stream during a typical day of operation. These flow rates are dependent on a number of factors such as bagasse import rates and plant operating conditions. The quality parameters for this mixed stream during the period over which the research was done were as shown in Table 5.

Table 5: Properties of wastewater stream.

	Total COD	Soluble COD	TSS	pH
Units	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	
Average	11441	5026	2356	5.37
Maximum	15775	7575	5226	6.06
Minimum	7775	3240	1024	4.84

3.2 Determination of acid production from molasses

To determine the required molasses dosing rate it was necessary to determine the amount of VFA that could be produced from a given quantity of molasses and the impact of the VFAs produced on wastewater pH. From this the theoretical dosage rate requirement could be determined. VFA production potential was calculated from theoretical principles earlier forming a basis upon which to compare the empirical result obtained here.

Operation

To determine the comparative titration curves for acetic acid and VFAs produced from molasses, a culture was fermented overnight using 10 g of molasses diluted in 1 l of water. The VFA concentration was determined and titration curves drawn for the culture produced and an acetic acid solution.

The VFA yield of molasses, as g acetic acid per g molasses, was empirically determined by allowing a $1g.l^{-1}$ solution of molasses to ferment until a stable pH was achieved after which the VFA concentration was measured. This was compared to the theoretical yield reported earlier.

3.3 Batch acidogenic solids removal

Apparatus

Batch tests were done using closed reactors suspended in a water bath that was thermostatically controlled at 37°C.

Operation

Each reactor was filled with wastewater with a backwater:reclamation water ratio of 2:1 and charged with the relevant additive as follows:

- Molasses was dosed at 0, 667, 1000 and $1333mg.l^{-1}$.

- Starch was added at 0, 667, 1000, 1333 $mg.l^{-1}$ as dry solids.
- Urea was added at 0, 153 , and 311 $mg.l^{-1}$ as N content.
- Phosphoric acid was added at 0, 53 and 107 $mg.l^{-1}$ as P.

One set of tests was done in which backwater:reclamation water ratios of 5:1, 2:1 and 1:1 were used. For batch tests in which molasses was not used as a variable molasses was added at I $g.l^{-1}$. Urea and phosphoric acid were not added to the reactors in which they were not used as variables.

The reactors were closed before being immersed in the water bath for 18 hours. After the reaction period, the supernatant was collected from each sample and tested for COD and TSS. Sludge was collected from some of the samples for sludge solids determination.

In some cases the clarification in particular batches was poor. After sample collection, acetic acid was titrated into the reactors to adjust the pH to 5, before being allowed to react in the water bath for a further hour, to determine if pH adjustment would induce coagulation and clarification. This was done to determine the impact of pH on reactor performance and to determine if acid addition could be used as a means of performance control.

3.4 Continuous acidogenic solids removal.

Introduction

During operation of the continuous acidogenic solids removal system, the following operational parameters were determined:

1) The effect of COD load on TSS and COD removal performance, as COD load is used as a measure of the capacity of biological reactors (Marais & Ekama 1984) and is used to determine the size of reactor required for full scale operations.
2) The pH in the acidogenic reactor as it is seen as critical to the performance of acidogenic solids removal systems (Zeeman *et al.*, 1997).
3) The use of acetic acid addition as a means of controlling reactor performance by ensuring a pH less than 5.5 is reached in the acidogenic reactor.

Apparatus

Apparatus used for the continuous acidogenic solids removal process, including the acidogenic continuously stirred tank reactor (CSTR) and the sludge settler, is illustrated in Figure 2.

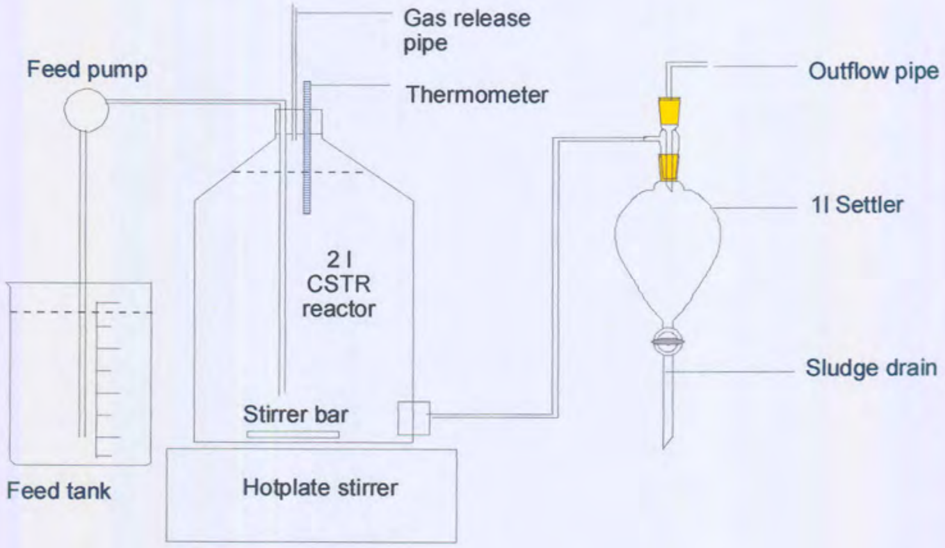

Figure 2: Acidogenic CSTR reactor and settler arrangement.

Operation

Because this research was done to develop a treatment system to handle wastewater from the mill, no attempt was made to manipulate the backwater:reclamation water ratio of the samples collected so that the effect of the variability of the wastewater on the system would be observed.

A 15 l sample of wastewater was collected each day. The sample was allowed to stand for an hour to allow settleable solids settle out before the supernatant was sieved though a 100μm screen to remove any remaining fibres. (This was done to protect the pump, which otherwise became blocked by fine suspended fibres, rather than as a process requirement.)

As described later, a molasses-dosing rate of 1.3 $g.l^{-1}$ produced the best TSS removal results but a dose of $1g.l^{-1}$ was recommended to minimise inorganic salt addition. Furthermore, preliminary CSTR work showed that a dosing rate of $1mg.l^{-1}$ was sufficient. Carbohydrates and other readily biodegradable organic compounds in the mill wastewater made up for the reduced molasses addition.

Urea and phosphoric acid were added at addition rates of 156 mg $N.l^{-1}$ and $53mg.l^{-1}$ respectively in accordance with the results obtained from the batch tests. This ensured a COD:N:P ratio of 100:1.4:0.5 relative to average feed COD, which is well above the ratio found by Qiu *et al.* (1987) of 100:1.2:0.1 to be sufficient for UASB feed.

The reactor feed tank was then emptied, cleaned and filled with the fresh wastewater. Wastewater was pumped from the feed tank into the acidogenic reactor at the designated addition rates, which during the course of the tests were varied to give hydraulic retention times of 4, 6 and 12 hours. Combined with the variability of the feed COD, the changes in feed rate ensured a range of COD loading rates of between 14 and 86 $kgCOD.m^{-3}.d^{-1}$. The reactor was maintained at a temperature of 37°C by the hotplate that was manually adjusted according to the temperature reading on the thermometer.

Effluent from the acidogenic reactor passed through the settler into the methanogenic reactor. Sludge from the settler was drained out daily. The system was run in conjunction with the subsequent methanogenic and aerobic reactors for 8 weeks.

The following samples were collected daily (except over weekends) and analysed for TSS, COD and pH.

1) Fresh feed after molasses addition.
2) Acidogenic mixed liquor suspended solids MLSS.
3) Settler supernatant.
4) Settler sludge.

When the acidogenic reactor failed to produce settleable flocs, due to low reclamation water content in the wastewater, the acidogenic reactor feed pH was adjusted to 6 using acetic acid. This was found to be sufficient to allow the pH to drop low enough (pH 5 to 5.5) for coagulation to occur in the acidogenic reactor. The results obtained on these occasions were excluded from the results reported.

3.5 Anaerobic/aerobic treatment of acidogenic effluent

3.5.1. Methanogenic treatment

Apparatus

Apparatus used for the methanogenic UASB treatment stage is shown in Figure 3.

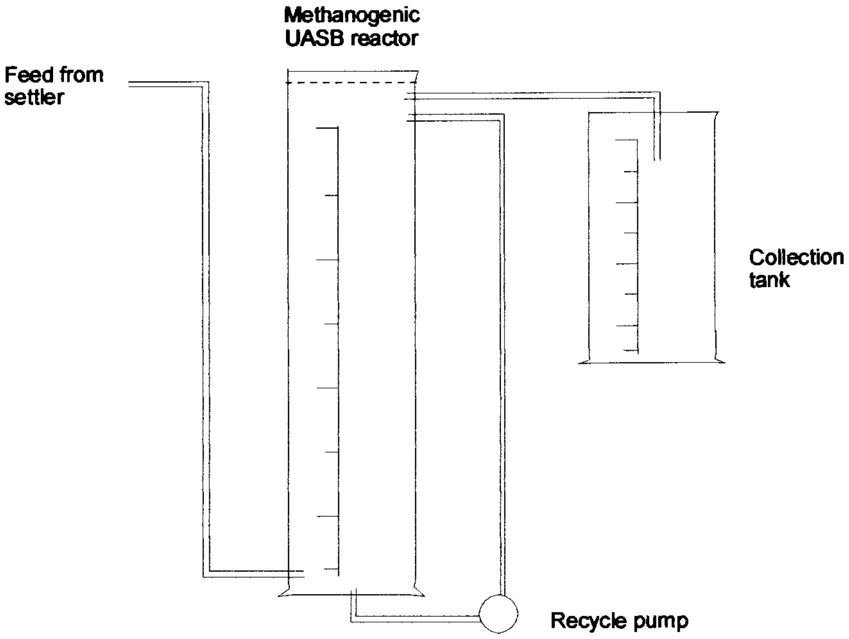

Figure 3: Methanogenic UASB reactor configuration.

Operation

Effluent from the acidogenic stage settler flowed by gravity into the methanogenic stage. An external pump was used to circulate effluent from the UASB to mix with the feed coming from the acidogenic system at a rate sufficient to fluidise the sludge bed. 1500ml of pelletised sludge, obtained from a brewery effluent treatment UASB reactor, was added. The pelletised sludge adapted well to the acidogenic effluent, producing methane within fifteen minutes of start up.

Adjustment of the acidogenic effluent feed pH entering the methanogenic reactor was achieved by dilution with recycle from the methanogenic effluent. In this way the pH in the methanogenic reactor was kept relatively stable.

Hydraulic retention times were as for the acidogenic reactor as they were both 2 l vessels. COD loading rates are given in the results. COD loading rates are as given in Table 6.

Table 6: Anaerobic reactor COD loading rates.

Measure of COD loading rate	Methanogenic reactor	UASB reactors in Pulp and Paper industry
kg COD/kg MLSS/d	1.17 to 8.86	7 to 10
kg COD.m-3.d-1	8.7 to 66.5	6 to 24
Reference		Lee *et al.* 1989

Effluent from the methanogenic stage was collected for addition to the aerobic reactor. A daily sample of the effluent was taken for analysis. A sludge sample was collected for gravimetric MLSS determination.

3.5.2. Aerobic treatment

Apparatus

Apparatus used for the aerobic activated sludge SBR is shown in Figure 4.

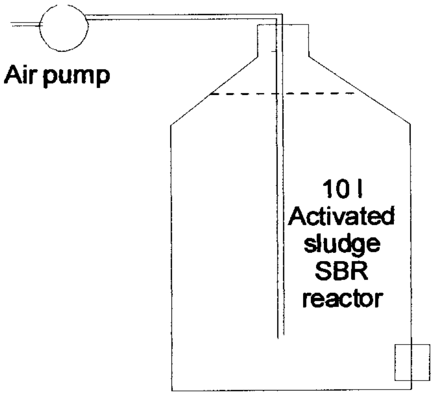

Figure 4: Activated Sludge Sequencing Batch Reactor (SBR)

Aerobic stage method

The aerobic activated sludge SBR was inoculated with 2 l of activated sludge from a sewage treatment plant. It was run on a 24-hour cycle being stopped for an hour each day to allow sludge to settle. 8 l of supernatant was drained off after settling. The supernatant was replaced with fresh feed collected from the methanogenic reactor. A sample of the supernatant was taken for TSS, COD and pH analysis. Aeration was started at an air addition rate of 1.2 l air per l reactor per minute. The reactor was housed in a laboratory in which the ambient temperature was controlled at between 23 and 25°C. The COD loading rate range is given in Table 7.

Table 7: Aerobic COD loading rates.

Measure of COD loading rate	Aerobic reactor	Activated sludge reactors in Pulp and Paper industry
kg COD/kg MLSS/d	0.4 to 0.88	0.4 to 1
kg COD.m-3.d-1	1.2 to 2.66	> 3.2
Reference		Springer, 1993

Samples (100ml) were collected weekly for MLSS determination.

3.6 System performance

The performance of each stage of the processes and the overall system performance were evaluated in terms of TSS and COD removal. The final effluent quality was assessed against water quality requirements of the mill to determine if it could be used as reclaimed water.

3.7 Analytical Test Methods

The following tests and test methods were used:

1) Measurement of pH was done using a standard pH electrode and meter.
2) Total suspended solids (TSS) was determined using TAPPI test method T 656 (TAPPI Test Methods 1998-1999). This involves a gravimetric measurement of solids filtered from a set volume of water.
3) The four point VFA and alkalinity titration method given by Moosbrugger et al. (1992) was used.
4) COD was measured using Hach Photospectrometer Method 8000 (Hach, 1988: 445).
5) MLSS was measured as reactor content TSS using method 2 above.
6) Sludge solids content was determined as percent TSS per unit sample volume.

4. Results and Discussion

4.1 Acid production from molasses

Titration

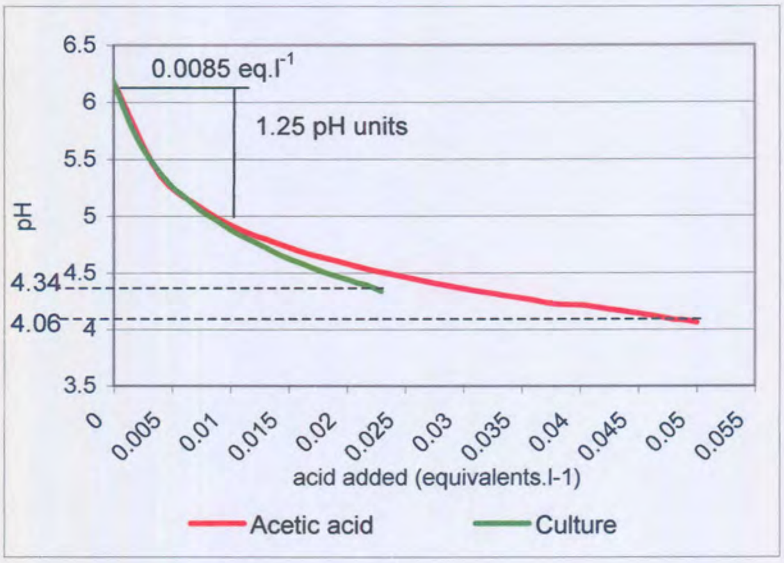

Figure 5: Titration curves of acetic acid and an acidogenic culture fed with molasses showing the VFA equivalents needed to drop the pH to 5 for effective solids separation.

Figure 5 show a comparison between the titration curves for acetic acid and acidogenic culture, fermented from a 10 g.l^{-1} solution of molasses in water, titrated into wastewater. The culture produced a pH of 4.06 with a volatile fatty acid (VFA) concentration of 2580 mg.l^{-1} as acetic acid equivalents. Both the acetic acid and acidogenic culture VFA concentrations in the titrant were calculated and given on the graph as equivalents.l^{-1}. The titrant VFA concentration required to lower the pH to 5, the pH below which acidogenic solids removal worked optimally (see results for batch and continuous acidogenic solids removal) is indicated on the graph. Since the wastewater pH during the period over which this work was done seldom exceeded 6, this is considered to be a maximum estimate of VFA requirement. Titration results are given in Appendix 1.

Deviation of the acetic acid and "culture" titration curves is thought to be due to the presence of non-volatile organic acids in the culture.

4.1.1. VFA production

Complete fermentation resulted in 390mg.l^{-1} of VFA produced per 1g.l^{-1} of molasses added. This is less than the 439mg.l^{-1} acetic acid yield predicted through theoretical calculations reported earlier. Losses in acetic yield are due to:

- The presence of oxygen in the dilution water resulting in some VFA metabolism;

- Conversion of sugars to higher molecular weight VFAs such as propionic and butyric acids; and
- Discrepancies between the theoretical and actual cell yield coefficient a_e for the reaction.

A VFA concentration of 390mg.l^{-1} converts to an equivalents concentration of 0.0065 equivalents.l^{-1}. A molasses dosage rate of 1.3g.l^{-1} would produce a VFA concentration of 0.0085 equivalents.l^{-1}, which according to the titration curve in Figure 5, would account for a drop in pH from 6.25 down to about pH 5. Since this is within the required pH range for coagulation to take place in the acidogenic reactor, a theoretical dosing rate of 1.3g.l^{-1} was targeted, and found to be more than adequate with a dosing rate of 1g.l^{-1} being preferable as discussed later.

4.2 Batch acidogenic solids removal

The results of the batch tests done to determine the effect of the identified parameters on the acidogenic solids removal reaction are given below. Results shown are averages from the sets of results obtained. The detailed results for batch tests are given in Appendix 2.

4.2.1. Molasses

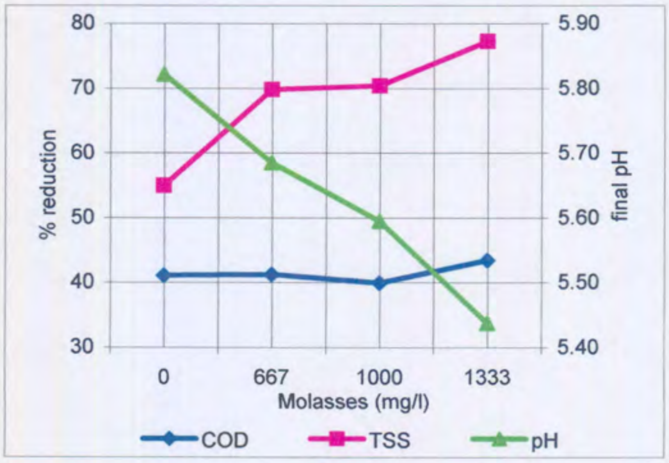

Figure 6: Percent COD and TSS reduction and pH change with increased molasses addition.

Figure 6 shows that molasses dosage was of value in improving TSS reduction, as the TSS removal rate improved from 55% without molasses to 78% with molasses dosed at 1.33 g.l^{-1}. The pH results for these tests showed a decrease in pH with higher molasses addition, which accounts for the benefits that were observed. The COD reduction curve indicated very little impact of increased molasses dosing possibly due to the COD content of the molasses added.

The batch tests show that reactor performance improves with increasing molasses addition. Although better results are obtained with 1.33g.l^{-1} than at 1g.l^{-1}, it is acknowledged that the molasses dosing should be limited as molasses contains undesirable inorganic constituents (approximately 38% by mass according to the supplier). For this reason a dosing rate of 1 g.l^{-1} was considered preferable for further work.

Starch addition was found to be ineffective and was not investigated further.

4.2.2. Feed ratio

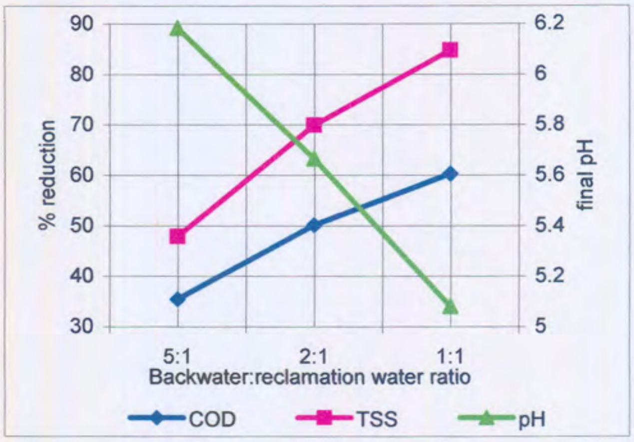

Figure 7: COD and TSS reductions and pH changes with increasing feed reclamation water proportion.

Figure 7 illustrates that increasing the reclamation water ratio increased the COD and TSS reduction potential of the reaction relative to total concentrations in the wastewater mixtures used. This can be ascribed to lower initial pH values that resulted in lower final pH values as shown in Figure 7. Since the reclamation water contains Ritter water, washed from the stored bagasse, increasing the reclamation water proportion also increased the acidogenic bacteria population at the start of the reaction contributing to reactor performance.

These results show that under operational conditions which limit the flow of reclamation water to the wastewater stream the acidogenic solids removal stage can be expected to be less effective and implies the need to apply a means of controlling the reactor performance.

4.2.3. Urea

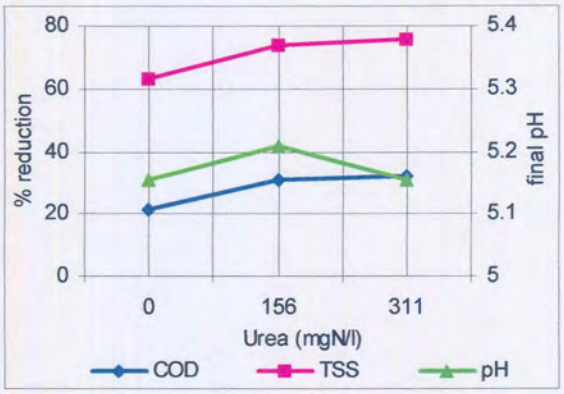

Figure 8: COD and TSS reduction and pH changes with increasing urea addition.

Figure 8 shows the results obtained from the urea tests and illustrates that urea effected a definite improvement in COD and TSS reduction. However, addition of 156 mg/l (as N) is sufficient as the higher dosing rate resulted in little further improvement in performance. The fact that pH is higher for the sample with 156 mg $N.l^{-1}$ indicates that improved TSS removal is not only a function of pH but is also due to a biological requirement for nitrogen in the reactor. Taking the initial COD value for the batch of $11800 mg.l^{-1}$, this rate gives a COD:N ratio of 100:1.3 which is close to the 100:1.2 used by Qiu *et al.* (1987) for their anaerobic system.

4.2.4. Phosphate

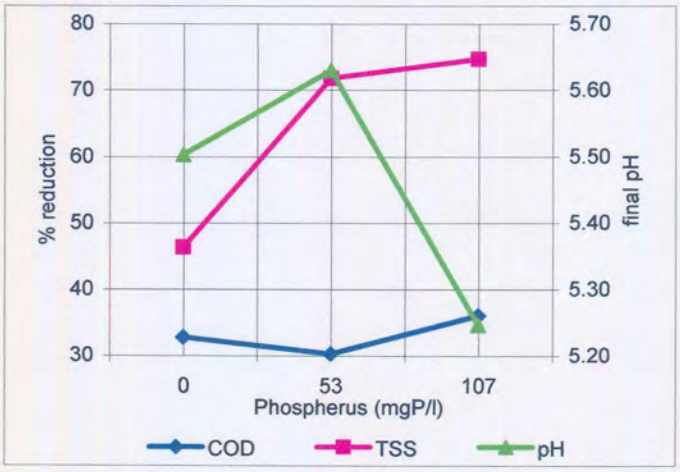

Figure 9: COD and TSS reductions and pH changes with increasing phosphate addition.

From Figure 9 it can be seen that a small (53 mg/l as P) addition of phosphoric acid had a highly significant impact on the performance of the reactor. The higher addition rate added little to this improvement. As for the urea addition results, performance did not relate to final reactor pH indicating that the improvement due to a requirement for phosphate. Since the initial COD was 11800mg.l-1 this dosing rate COD:P ratio is 100:0.45 which is higher than the 100:0.1 given by Qiu *et al.* (1987) for their UASB reactor.

4.2.5. Effect of pH

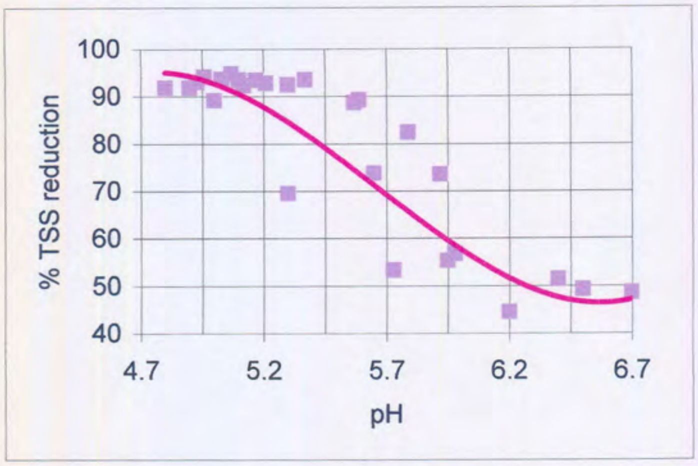

Figure 10: TSS reduction vs. pH.

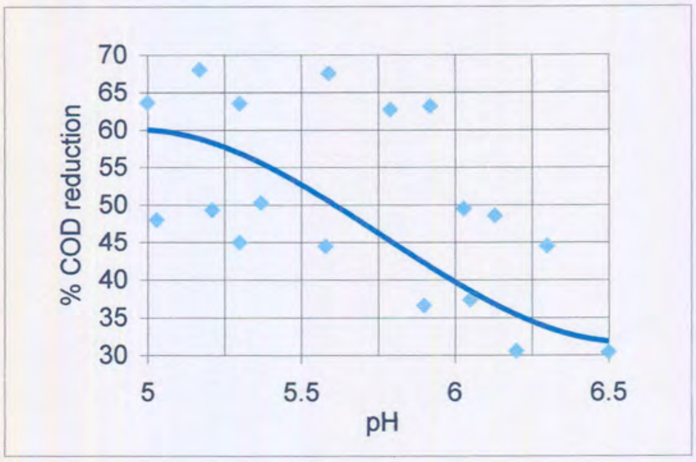

Figure 11: COD reduction vs. pH.

Figure 10 and Figure 11 were compiled from combined data of all batch tests done, and show the increase in TSS and COD reductions in samples as the pH drops from 6 to 5.25. (Both graphs are drawn using a 3rd degree polynomial best-fit plot.) This is particularly true for TSS, which shows very stable reduction at just over 90% below pH 5.25. The trend applies to COD reduction largely due to removal of particulate COD.

Batch tests showed that pH is a critical factor in determining the effectiveness of the acidogenic stage as a solids removal step. Addition of molasses, higher reclamation water ratios and acetic acid all caused a drop in pH and led to improved reactor performance. The batch test also showed the reaction could be improved to some extent by the addition of nitrogen, in the form of urea, and of phosphate. However, the flocculation time was 12 to 18 hours (approximately 20 to 30 kg COD.$kl^{-1}.h^{-1}$). This could possibly be improved by continuous stirring to increase the velocity gradient in the reactor.

4.2.6. Acetic acid addition

In a number of batch reactors throughout the batch trials coagulation and settling failed to take place. In all cases, the pH was found to be above 5.5. Addition of acetic acid to adjust the pH to 5 induced coagulation in these reactors within an hour. (These results were excluded from the results reported above.) This confirms the importance of pH in the process and shows that pH adjustment can be used to control the performance of the reaction. In full-scale operation the feed to the acidogenic reactor is variable as discussed earlier. The implication is that under certain conditions, the feed may not have a sufficiently low pH and the reactor will fail. Under these circumstances, pH adjustment using acetic acid could be used to ensure reactor performance.

4.2.7. Summary of batch results

- Molasses addition at 1 g.l^{-1} is recommended to optimise the benefits gained.
- Backwater to reclamation water ratio affects wastewater pH, and therefore the reactor performance, such that high ratios can be expected to result in poor performance. Monitoring of the wastewater pH is therefore recommended so that pH adjustments can be made to ensure reactor performance. Control of feed pH is discussed later.
- Combining the urea and phosphate results gives a COD:N:P ratio requirement of 100:1.2:0.45 in the acidogenic CSTR.
- The effect of pH shows that pH control is seen as critical in ensuring acidogenic solids removal performance.

4.3 Continuous acidogenic solids removal

Results for continuous acidogenic, methanogenic and aerobic treatment work are reported in Appendix 4.

4.3.1. Effect of COD load

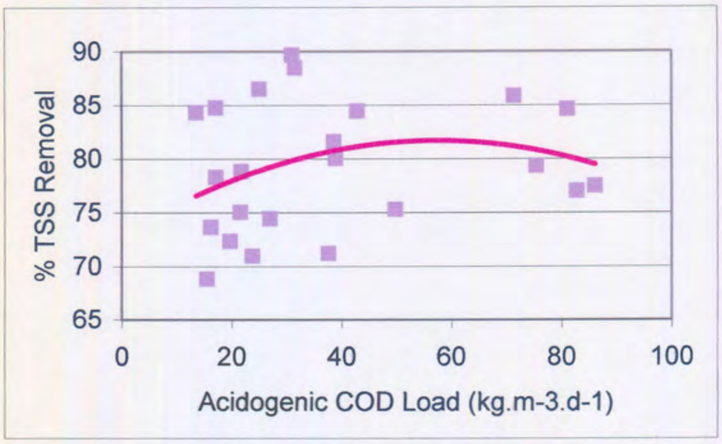

Figure 12: % TSS removed vs COD load

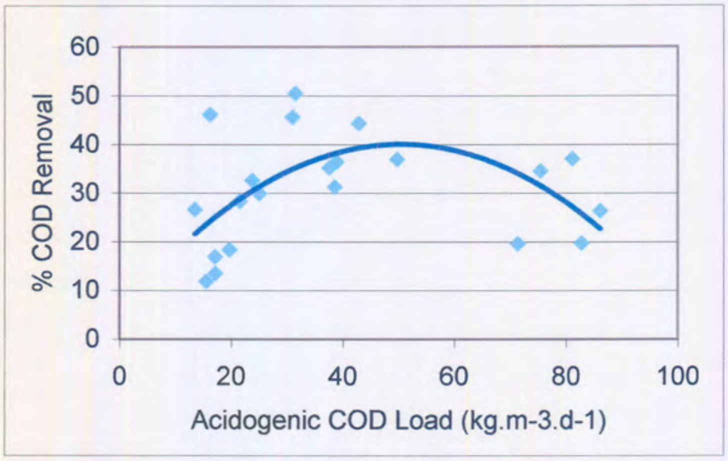

Figure 13: % COD removed vs. COD load

Figure 12 and Figure 13 indicate that the optimum COD load in the acidogenic stage is in the range between 50 and 60 kg.m^{-3}.d^{-1}. (The use of the more conventional load measure of kg COD/kg MLSS was not used in this instance since the sludge was not allowed to accumulate). In terms of soluble COD, which was on average 44% of total COD fed to the reactor, the COD load above would be 22 to 26.4 kg soluble COD.m^{-3}.d^{-1}. This is close to the 28 kg soluble COD.m^{-3}.d^{-1} load reported by Speece (1997) for a starch wastewater acidogenic stage reactor.

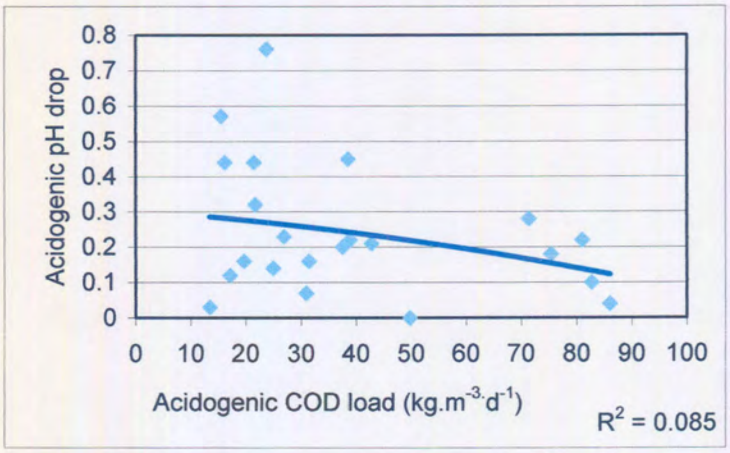

Figure 14: Acidogenic pH drop vs. COD load.

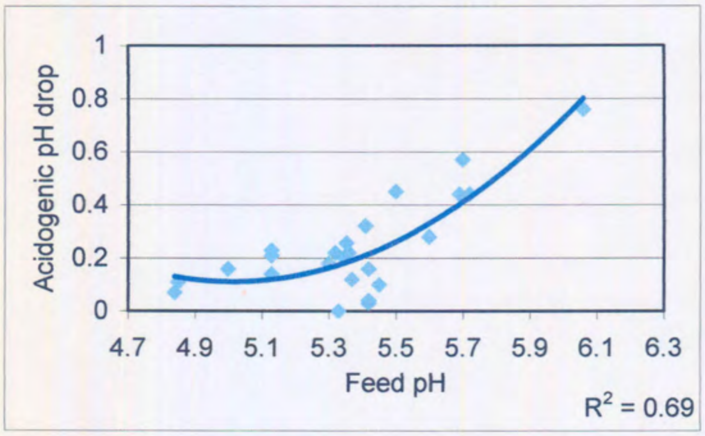

Figure 15: Effect of feed pH on pH drop in reactor.

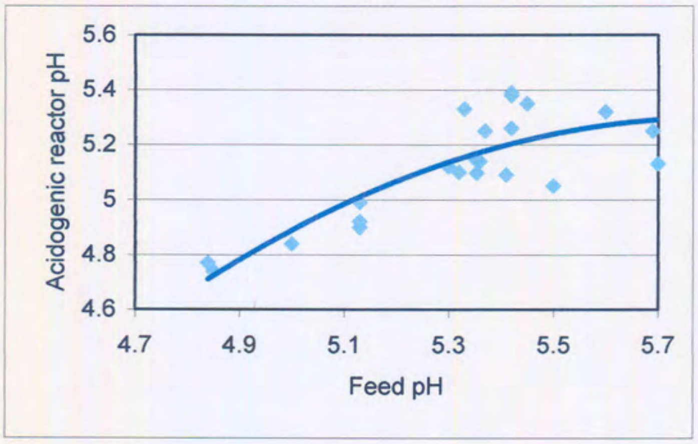

Figure 16: Acidogenic reactor pH vs. feed pH.

Figure 14 shows that the COD load did have some effect on the pH drop in the reactor but the degree of scatter (R^2 correlation with binomial best fit of 0.085) indicates that other factors, such as feed pH, as indicated in Figure 15 (R^2 = 0.69), had a greater effect. The comments on the effect of load on TSS and COD removal should therefore be seen as subject to wastewater conditions being within the range reported in this work.

Figure 15 indicates that the acidogenic reactor pH drop was higher at higher feed pH levels. This is due to the presence of higher concentrations of anaerobically biodegradable organics in the backwater, which forms a higher proportion of the feed at higher feed pH levels. Despite this improved pH drop, Figure 16 shows that the reactor pH is higher at higher feed pH levels showing that addition of acid, or more biodegradable organic sources for conversion to VFAs, would be required if feed pH levels rise too high. The use of acetic acid for this purpose, during this experimental work, is discussed later.

4.3.2. Effect of pH

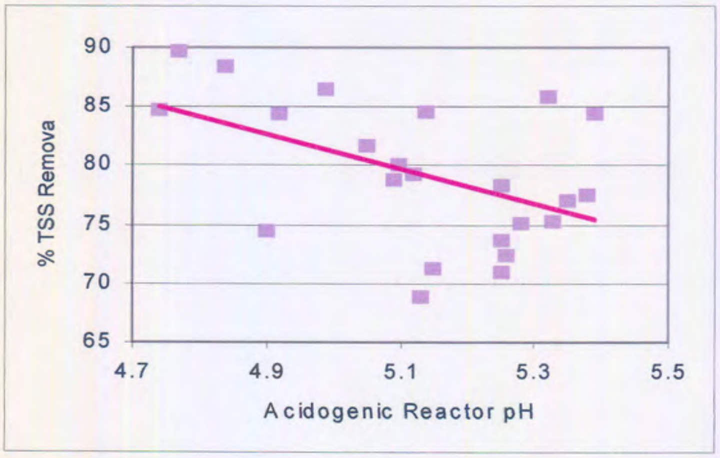

Figure 17: TSS reduction vs Reactor pH

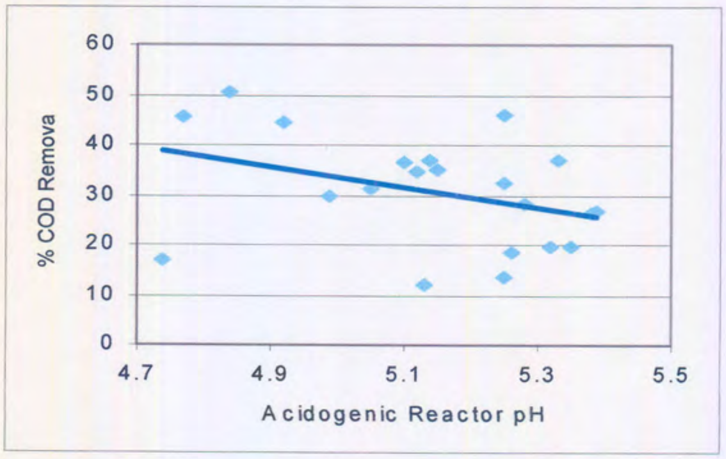

Figure 18: COD reduction vs Reactor pH.

Figure 17 and Figure 18 show that the TSS and COD removal rates increase at lower reactor pH levels. As for the batch tests, this shows that control of pH is critical to the operation of the system.

4.3.3. Comments on comparative batch and continuous reactor performance

Acetic acid addition

Acetic acid was used to lower the pH to 5 in a number of batch reactors in which the reaction had failed to produce acceptable results. In all cases, the solids precipitated out after allowing the reaction to continue for a further hour in the water bath.

During the continuous reactor work, similar tests were done on a few days when the reactor performance was poor due to high feed pH levels, which caused the reactor pH to rise above 5.5. Acetic acid was added to the feed to bring the pH below 6 and the solids separation increased to normal levels within one hydraulic retention time in all cases. These tests indicated that pH adjustment of the reactor, or the feed to the reactor, could be used to control reactor performance. Apart from using acetic acid, which would be costly, an acidogenic molasses culture or simply an increase in molasses dosing could be used to achieve the same results.

It should be noted that in both the batch and continuous reactor work the results obtained after addition of acetic acid were excluded from the results tables.

Supernatant

The pH of batch test supernatant had to be corrected to 6.5 before it could be added in batch form to a methanogenic reactor as methanogenesis is inhibited below pH 6.5. This was not required for the supernatant from the continuous reactor as it was fed continuously to the methanogenic reactor and diluted and neutralised with the recycle flow used to fluidise the bed. TSS levels after the continuous process were lower averaging 464 mg.l^{-1} while in the batch tests the final TSS was often between 1000 and 4500 mg.l^{-1}.

Residence time

Batch tests were very effective in reducing TSS and COD in the supernatant if the pH dropped sufficiently during the reaction. However, the reaction times were very long, requiring that they be left overnight (18-hours) before testing. Comparing this to the six hours required by the continuous reactors, it is thought that mixing enhances the reaction due to better contact between the sludge and liquor. Sludge activity is also enhanced by the microbial selectivity of the CSTR system that selects for organisms best suited to the conditions in the CSTR.

The above comparison shows that the continuous acidogenic solids removal system outperformed the batch system due largely to mixing increasing contact between substrate and microbes, and improving sludge solids content due to the velocity gradient in the CSTR. Mixing in batch reactors would help overcome these differences but the addition of low pH supernatant in batches to a subsequent methanogenic reactor would remain problematic because the low pH would inhibit methanogens. This could be overcome by: adding a base to raise the pH, which would increase running costs; or by collecting the supernatant in a vessel, which would add to the capital cost, and feeding it continuously into a methanogenic reactor. The CSTR is therefore the preferred technology.

4.4 Methanogenic and aerobic treatment

The acidogenic effluent responded well to anaerobic and aerobic treatment because the TSS to COD ratio had been reduced from 21% in the wastewater to 6 % in the acidogenic system effluent. This is particularly significant for the Methanogenic UASB reactor for which a TSS to COD ratio of less than 10% is recommended (Lettinga & Hulshof Pol, 1991).

The effect of COD load on both the methanogenic and aerobic systems used are discussed below.

4.4.1. Effect of COD load on the Methanogenic reactor

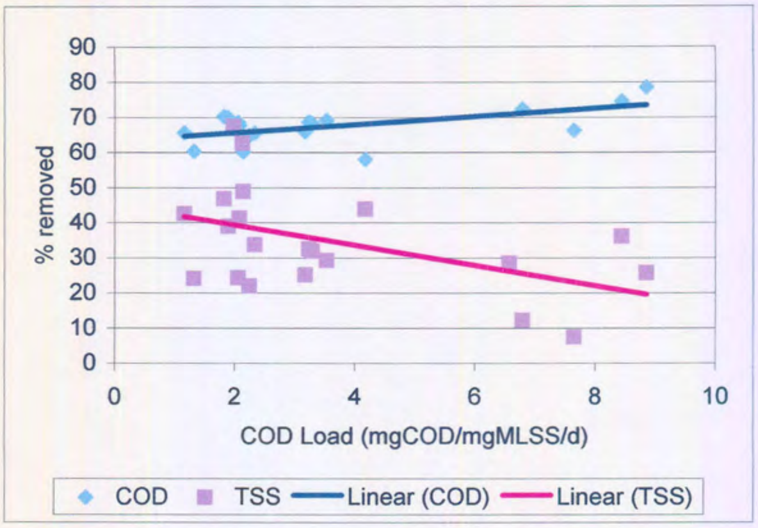

Figure 19: COD and TSS removal vs. COD load in the methanogenic reactor.

Figure 19 shows that, although COD removal increases marginally, TSS removal decreases with higher COD load. This is not considered to be a problem as the primary purpose of the methanogenic stage was COD removal not TSS removal. Furthermore, retention of suspended solids is not desirable in this stage, as it would result in an accumulation of inert solids in the reactor sludge. Inert solids accumulation is particularly undesirable in anaerobic reactors because of the long sludge ages during which inert solids can accumulate.

4.4.2. Effect of COD load on the Aerobic reactor

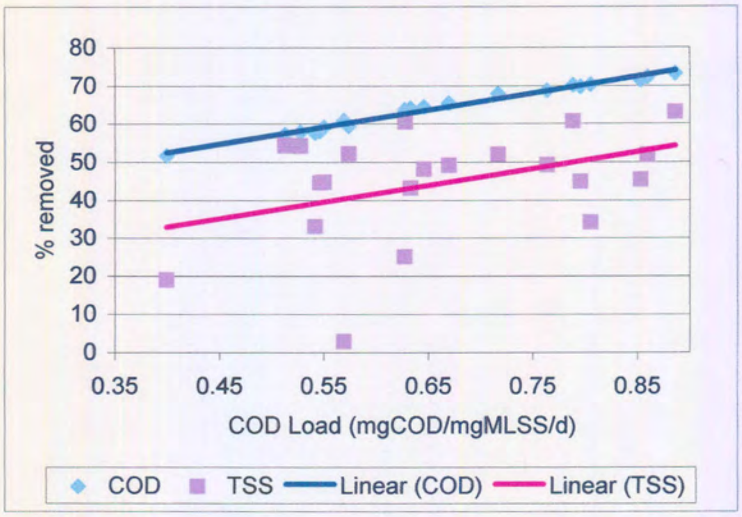

Figure 20: COD removal vs. load in the aerobic reactor.

As seen in Figure 20, both COD and TSS removal rates in the aerobic reactor increase with increasing COD load. The correlation between COD load and percent COD removal suggests that the higher COD levels were largely due to biodegradable COD passing through the methanogenic reactor at higher loads. TSS removal also increased due to floc formation of the anaerobic sludge. Accumulation of inert solids in the reactor sludge was not found to cause problems as the sludge age was only in the region of 15 days, limiting the time for inert sludge accumulation.

4.5 Overall System performance

4.5.1. Changes in pH

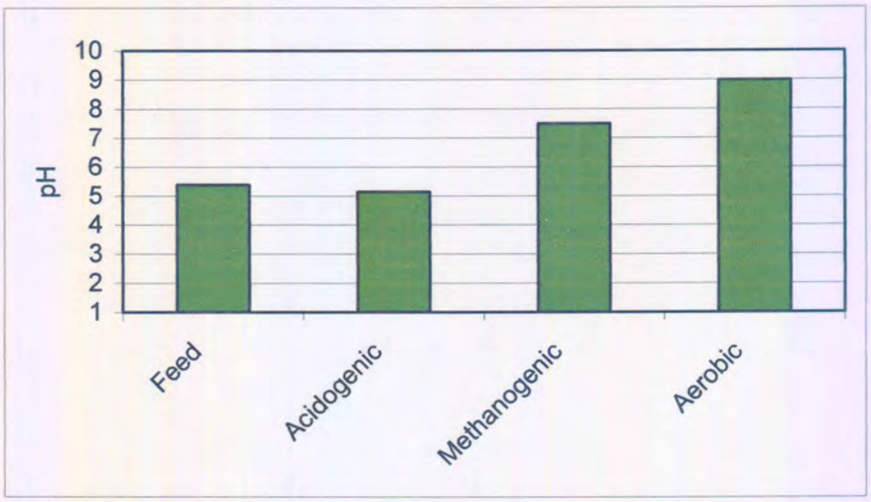

Figure 21: Changes in pH after each stage of the process.

Figure 21 shows how the pH dropped in the acidogenic stage due to VFA production but increased again in the methanogenic and aerobic stages as the VFAs were metabolised. The increase in pH as VFAs were metabolised was due to residual sodium in the water from the bagasse cooking process.

The high final pH is not considered problematic with respect to reuse of the water by the mill, as it would not affect the process or equipment significantly. The only possible impact would be in pulp washing applications where the high pH would reduce water drainage from the pulp due to increased viscosity at higher pH. Lowering the pH by adding carbon dioxide to the reclaimed water before application in the pulp washers would overcome this problem.

The high final pH would disqualify the effluent from disposal into local surface waters. Disposal at sea through the current system would be acceptable as the permitted pH range is 5 to 9.5. However, if plans to incinerate the black liquor do not materialise the combined wastewater stream would have a pH in excess of 9.5 and would require acid addition before disposal.

4.5.2. TSS reduction

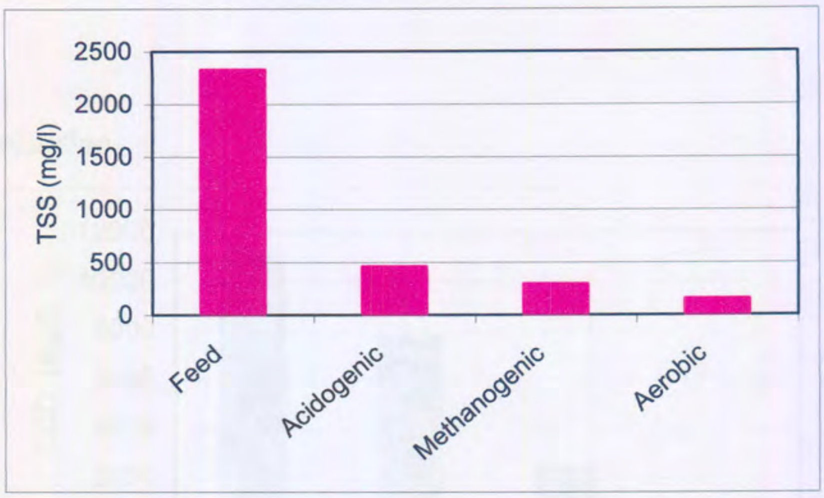

Figure 22: TSS after each stage of the process

Figure 22 shows the decrease in TSS levels throughout the process, while Table 8 gives the total percent reduction in TSS and COD relative to the initial feed (*cumulative*) and for the specific reactor (*reactor*), for each stage based on average results. It is evident that the acidogenic process results in 80% of the decrease in TSS while methanogenic treatment and aerobic treatment increase the cumulative TSS reduction to 87 and 93 % respectively. To achieve this the methanogenic reactor only reduced TSS passing through it by 36 % while aerobic treatment reduces TSS through it by 48%.

The final TSS of 153 mg.l^{-1} is considered too high for spray and glandservice applications as the mill uses water with less than 50 mg.l^{-1} TSS as per spray nozzle supplier recommendations. Use of pressure filters has been commonly used to treat reclaimed water for these applications (Webb, 1997). Pulp dilution and wash water do not have such restrictions and this final effluent would be acceptable in terms of TSS for these applications.

If the effluent were disposed of into the current pipeline the mills compliance with the permitted TSS concentration of 5000 mg.l^{-1} would be guaranteed even if the black liquor were still included in the flow, as the black liquor TSS concentration has not been recorded to exceed 5000 mg.l^{-1}.

4.5.3. COD reduction

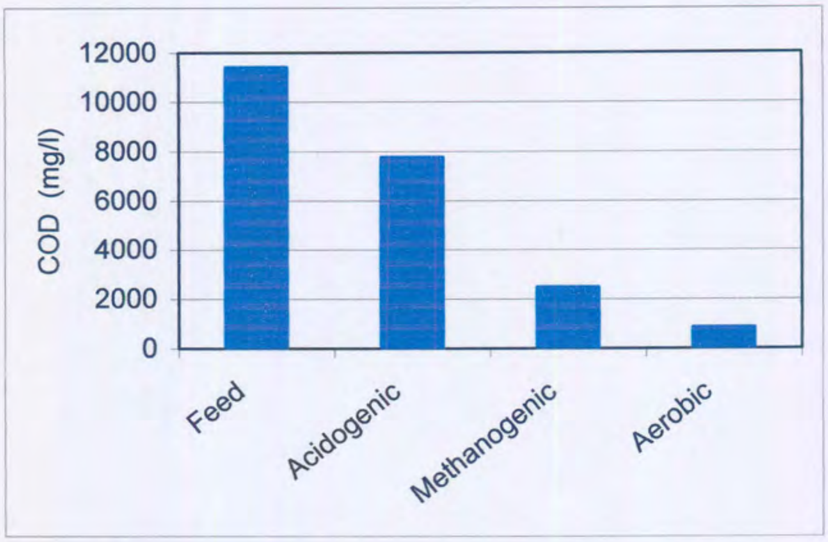

Figure 23: COD after each stage of the process

Changes in COD concentration throughout the system are shown in Figure 23. Although COD reduction in the acidogenic reactor is not as high as TSS reduction, COD reduction is higher in the methanogenic and aerobic systems than the corresponding TSS reductions. Table 8 shows that the cumulative COD reduction is also 93% but stage specific methanogenic and aerobic COD reduction rates are 68 and 65 % respectively.

Table 8: Reduction in TSS and COD.

		Feed	**Acidogenic**	**Methan-ogenic**	**Aerobic**
Average TSS mg.l^{-1}		**2327**	**461.3**	**295**	**153.3**
% Reduction	Cumulative		80	87	93
	Reactor		80	36	48
Average COD mg.l^{-1}		**11550**	**7766**	**2482**	**862.4**
% Reduction	Cumulative		33	78	93
	Reactor		33	68	65

Since the COD load on the aerobic stage was low relative to other applications in the industry (see Table 6), it is assumed that the remaining COD was not readily biodegradable as biodegradable COD would have been consumed. This is important to the mill if the water is to be reclaimed, as introduction of biologically available COD into the water circuit causes slime build up as discussed earlier.

Disposal of the effluent into the current pipeline would be guaranteed the mills compliance with the permitted COD concentration of 21 000 mg.l^{-1}. Since the 900kl.d^{-1} of black liquor has a COD concentration of approximately 55 000 mg.l^{-1}, the mixed wastewater would have a COD concentration of about 15 600 mg.l^{-1} thus complying with permit conditions.

4.5.4. Design parameters

Based on the results obtained in the above investigations, the following tables of design specifications are proposed. These calculations are based on the maximum COD concentration measured in the wastewater during the continuous reactor trial, and on a maximum wastewater flow rate of 3000 kl.day^{-1}. Table 9 shows the calculation values for the acidogenic CSTR using spatial COD load, as there is no sludge recycle negating the use of MLSS as a design criteria.

Table 9: Design calculation for acidogenic CSTR.

	COD concentration	Flow	COD load	Optimum Reactor COD load rate.	Reactor volume
	mg/l	kl/day	kg/day	kg/m^3/day	m^3
Acidogenic reactor	15800	3000	47400	60	790

Table 10 shows the design values for the methanogenic and aerobic reactors using COD load on MLSS. A loading rate of 8 mgCOD/mgMLSS/day was selected for the methanogenic reactor to minimise the space requirement and TSS retention while staying within the range reported in the literature. A loading rate of 0.85 mgCOD/mgMLSS/day was selected for the aerobic stage as an initial optimum estimate within the range reported in the literature.

Table 10 : Design calculations for methanogenic and aerobic reactors.

	COD concentration	Flow	COD load	MLSS	Optimum Reactor COD load rate.	Reactor volume
	mg/l	kl/day	kg/day	mg/l	mgCOD/mgMLSS/day	m^3
Methanogenic reactor	11000	2800	30800	7500	8	5013
Aerobic reactor	3400	2800	9520	4000	0.85	2800

Detailed work on sludge settling indices (required for detailed settler design), activated sludge oxygen requirements, and sludge handling, fall outside the scope of this work. However, as an initial guideline for the acidogenic sludge settler, a surface are of 250m^2

would be sufficient at the flow rate given above, as the observed settling rate of the sludge from the acidogenic CSTR was greater than 0.5m.s^{-1}.

5. Conclusions

5.1 Acid production from molasses

Molassed was found to be an acceptable source of readily available organics for conversion to VFAs with a 1mg.l^{-1} aqueous molasses solution producing a VFA concentration of 390 mg.l^{-1} after acidogenic fermentation.

5.2 Batch acidogenic solids removal

Batch tests showed that pH is a critical factor in determining the effectiveness of the acidogenic stage as a solids removal step. The following could be concluded:

1) Molasses addition improved reactor performance by increasing the VFA concentration thereby decreasing reactor pH. Addition at 1g.l^{-1} produced good results though there was further improvement at 1.3g.l^{-1}. However, molasses does contain undesirable inorganic salt and should be used sparingly, making 1g.l^{-1} the preferred dosage.
2) Starch addition was ineffective.
3) As the proportion of reclamation water in the wastewater increased, reactor performance increased due to lower feed and final pH.
4) Nitrogen and phosphorus addition were found to be beneficial when dosed at 156 mg.l^{-1} and 53mg.l^{-1} respectively representing a COD:N:P ratio of 100:1.3:0.45.
5) Adjustment of reactor pH to 5 using acetic acid was effective in ensuring coagulation of solids in batch reactors showing that the reaction could be controlled.

5.3 Continuous acidogenic solids removal

Results from the continuous acidogenic solids removal system, and comparison of these with batch results, lead to the following conclusions:

1) The optimum COD loading rate was identified to be between 50 and 60 kgCOD/m^3/day giving TSS and COD reductions of approximately 82 and 40 % respectively.
2) The reactor performance was found to be dependent on the pH in the reactor. Adjustment of the feed pH to 6 using acetic acid was effective in ensuring satisfactory reactor performance again showing that the reaction could be controlled. Dosing with

an acidogenic molasses culture or simply increasing the molasses dosing level would produce the same result.

3) Comparison of batch and continuous acidogenic processes showed that the continuous reactor performed better because the stirring action in the CSTR ensured better contact between bacteria and substrate and supplies a velocity gradient that facilitated the formation of flocs with higher solids content.
4) Continuous feed of acidogenic effluent, from the settler attached to the acidogenic CSTR, to the methanogenic UASB reactor ensured that pH correction was maintained through circulation of UASB effluent. To achieve the same for batch reactors would require an intermediate holding tank from which to feed the UASB.

5.4 Anaerobic/aerobic treatment of acidogenic effluent

The optimum COD load for the methanogenic (anaerobic) stage was not clearly defined but due to decreasing TSS removal at higher loads a load of 8 mgCOD/mgMLSS/day was selected. At this load, the estimated TSS and COD reductions were 20 and 72 % respectively.

In the aerobic reactor, performance was proportional to COD loading rate within the range used in this study. A design loading-rate of 0.85 at which the estimated TSS and COD removal rates were 55 and 75 % respectively was selected.

More work on optimisation of the methanogenic and aerobic systems is required to define these loading rates more distinctly.

5.5 System Performance

With both TSS and COD removal of 93 % overall the system produced a final effluent which is acceptable for reuse in the mill except in spray and glandservice applications for which the water would have to be filtered. The effluent would also guarantee compliance with wastewater permit discharge conditions if disposed of though the current pipeline.

5.6 Design Criteria

Based on the results obtained, and on the maximum wastewater quality parameters and flow rate, the following minimum reactor sizes are recommended:

1. Acidogenic CSTR reactor	790m^3	
2. Acidogenic stage settler	250m^2	surface area
3. Methanogenic UASB reactor	513m^3	(MLSS = 7500 mg.l^{-1})

4. Aerobic SBR reactor	2800m^3	(MLSS = 3000 mg.l^{-1})

5.7 Need for further research

1) Optimisation of the methanogenic and aerobic stages. These were not the focus of this research and were therefore not fully optimised. Of particular concern are the nutrient and aeration requirement for the aerobic activated sludge system.
2) Determination of the mechanism of flocculation in the acidogenic reactor. This was beyond the scope of the research done.
3) Acidogenic sludge settling dynamics need to be investigated to determine more reliable settler design criteria.
4) Sludge handling and disposal methods need to be investigated.

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7. Appendices

7.1 Appendix 1

Calculations of VFA yield, as acetic acid, from molasses.

McCarty (1975) showed that a bacterially mediated reaction could be determined using the following equation:

$$R = R_d - f_e R_a - f_s R_c \qquad (1)$$

Where:

R = overall reaction
R_d = reaction of electron donor
R_a = reaction of electro acceptor
R_c = reaction of bacterial cell synthesis
f_e = fraction of electron donor going to electron acceptor
f_s = fraction of electron donor going to cell synthesis

By definition then:

$$f_e + f_s = 1 \qquad (2)$$

To calculate f_s the cell yield coefficient a_e must be calculated as follows:

$$a_e = \frac{1}{1+A} \qquad (3)$$

Where:

$$A = -\ \frac{\Delta G_p/k^m + 7.5}{K\Delta G_r} \qquad (4)$$

Where:

ΔG_p = $(\Delta G^o(W)_d + 8.54)$ and $\Delta G^o(W)_d$ represents the free energy per electrons equivalents for the electron donor reaction.

m = +1 if $\Delta G_p > 1$ and –1 if $\Delta G_p < 1$.

k = efficiency of energy transfer for bacterial growth approximated by 0.6.

ΔG_r = $(\Delta G^o(W)_d - (\Delta G^o(W)_a)$ in which $\Delta G^o(W)_d$ and $\Delta G^o(W)_d$ are the free energy per electrons equivalents for the electron donor and electron acceptor reactions.

Free energy per electrons equivalents for the electron donor (carbohydrate) and acceptor (acetate) half reactions for this reaction are given by McCarty (1975) as –10 and –6.609 respectively. The calculation of equation 4 and 3 are then:

$$A = -\frac{(-10 + 8.54)/0.6^{-1} + 7.5}{0.6(-10-(-6.609))} = 37.44 \qquad (5)$$

$$a_e = \frac{1}{1+37.44} = 0.027 \qquad (6)$$

McCarty showed that the cell synthesis fraction is calculate by the equation:

$$f_s = a_e\,(1-(f_d b t_s/(1+bt_s)) \qquad (7)$$

Where:

a_e = the cell yield coefficient calculated in equation 6.

f_d = the biodegradable fraction of micro organisms approximated at 0.8.

b = organism decay rate of approximately 0.03 day^{-1} for anaerobic organisms.

t_s = solids retention time which in this case is 0.25 day-1 as the acidogenic reactor is a continuously stirred tank reactor (CSTR) without sludge recycle meaning that the solids retention time is equal to the average hydraulic retention time of 6 hours.

Therefore:

$$f_s = 0.027(1-0.8\text{x}0.03\text{x}0.25/(1+0.03\text{x}0.25)) = 0.025 \qquad (8)$$

Therefore f_e is calculated from equation 2 as follows:

$$f_e = 1 - 0.025 = 0.975 \qquad (9)$$

The reaction in question is the conversion of carbohydrate to acerate so that the electron donor is carbohydrate and the electron acceptor is acetate. Urea, which is converted to ammonia, was used as a nutrient source in the acidogenic reactor. Using the f_s and f_c values calculated above and the half reactions given by McCarty (1975) the following half reactions are use in equation 1 for R_d, f_eR_a and f_sR_c.

R_d: $0.25\,CH_2O + 0.25\,H_2O = 0.25\,CO_2 + H^+ + e^-$ (10)

$-0.975R_a$: $0.122CO_2 + 0.122\,HCO_3^- + 0.975H^+ + 0.975e^- = 0.122CH_3COO^- + 0.366\,H_2O$ (11)

$-0.025Rc$: $0.005CO_2 + 0.001HCO_3^- + 0.001NH_4^+ + 0.025e^- + 0.025H^+ = 0.001C_5H_7O_2N + 0.0113H_20$ (12)

R: $0.25CH_2O + 0.123HCO_3^- + 0.001NH_4^+ = 0.122CH_3COO^- + 0.001C_5H_7O_2N + 0.123CO_2 + 0.127H_2O$ (13)

R: $1CH_2O + 0.492HCO_3^- + 0.004NH_4^+ = 0.488CH_3COO^- + 0.004C_5H_7O_2N + 0.492CO_2 + 0.508H_2O$ (13)

Hence 1 mol of carbohydrate yields 0.488 mol of acetate.

Therefore 30 g carbohydrate yields 0.488 mol x 60 g.mol^{-1} acetic acid

= 29.3 g acetic acid

Therefore 1g carbohydrate yields 0.976 g acetic acid

Meade and Chen (1977) report that molasses has an average carbohydrate content of about 56% by mass. The sugar mill from which the molasses was obtained reports a figure of 45% carbohydrate content. Therefore, 1g of molasses contains 0.45 g carbohydrates that will yield 0.439g acetic acid.

7.2 Appendix 2: Titration of wastewater with molasses culture and acetic acid.

Table 1: Acetic acid titration

Acetic	60	g/mol
Sample vol	50	ml
conc	0.10167	M
conc	6.1	g/l

Vol (ml)	Conc (M)	pH
0	0	6.18
2	0.00391	5.38
4	0.00753	5.08
6	0.01089	4.89
8	0.01402	4.77
10	0.01694	4.67
12	0.01968	4.6
14	0.02224	4.53
16	0.02465	4.48
18	0.02691	4.43
20	0.02905	4.39
22	0.03106	4.35
24	0.03297	4.32
26	0.03478	4.29
28	0.0365	4.26
30	0.03813	4.23
32	0.03967	4.22
34	0.04115	4.21
36	0.04256	4.19
38	0.0439	4.17
40	0.04519	4.15
42	0.04641	4.13
44	0.04759	4.11
46	0.04872	4.09
48	0.0498	4.08
50	0.05083	4.06

Table 2:Molasses addition

Molasses	60	g/mol
Sample vol	50	ml
conc	0.046667	M
conc	2.8	g/l

Vol (ml)	Conc (M)	pH
0	0	6.18
2	0.001795	5.74
4	0.003457	5.46
6	0.005	5.27
8	0.006437	5.15
10	0.007778	5.04
12	0.009032	4.96
14	0.010208	4.88
16	0.011313	4.82
18	0.012353	4.77
20	0.013333	4.72
22	0.014259	4.67
24	0.015135	4.63
26	0.015965	4.6
28	0.016752	4.57
30	0.0175	4.54
32	0.018211	4.51
34	0.018889	4.49
36	0.019535	4.47
38	0.020152	4.45
40	0.020741	4.43
42	0.021304	4.41
44	0.021844	4.4
46	0.022361	4.38
48	0.022857	4.36
50	0.023333	4.34

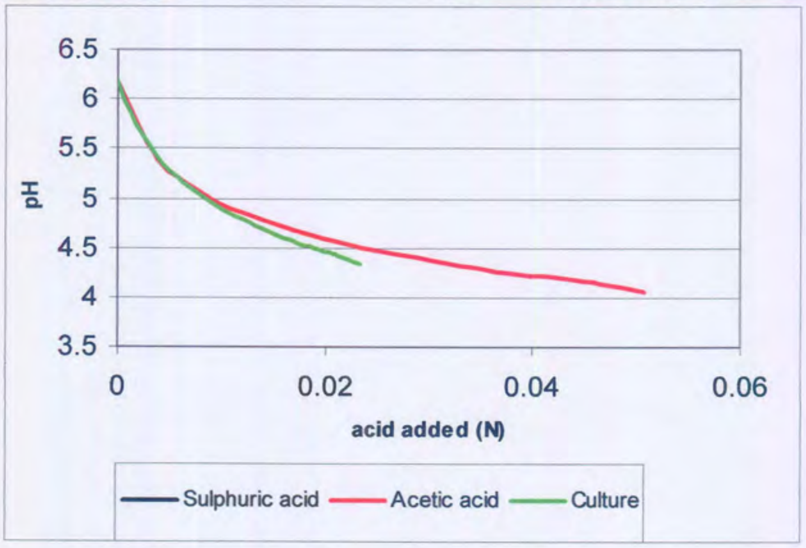

Figure 1: Titration curves.

7.3 Appendix 3: Batch test results

The raw batch test results are given in Table 1 and Table 2 below. The tests were done in a matrix of 11 reactors, as indicated by the tables, with each variable repeated accordingly. Some of the variables were disregarded for the purposes of the work reported, but are reflected here to complete the results for retained variables. Results reported in Table 3, and used in the text, are based on averages of the percent reductions of COD and TSS, and for final pH.

Table 1: Raw data from batch tests.

A

Molasses added (ml)

Ratio BW:RW	Start				End				Difference				Percent reduction			
pH	0	1	2	3	0	1	2	3	0	1	2	3				
05:01	8.24	8.24	8.24	8.24	6.92	6.7	6.5	6.4	1.32	1.54	1.74	1.84				
02:01	6.56	6.56	6.56		6.05	5.9	6.2		0.51	0.66	0.36					
01:01	6.15	6.15	6.15	6.15	5.58	5.3	5	4.8	0.57	0.85	1.15	1.35				
COD																
05:01	17650	18600	18250	17550	11200	12625	12700	12800	6450	5975	5550	4750	37	32	30	27
02:01	17400	17550	18550		10900	11125	12875		6500	6425	5675		37	37	31	
01:01	17700	19200	19750	20550	9825	7000	7175	6625	7875	12200	12575	13925	44	64	64	68
TSS																
05:01	6700	6600	6750	7250	3350	3400	3425	3525	3350	3200	3325	3725	50	48	49	51
02:01	8450	7550	8250		7125	7375	4575		1325	175	3675		16		45	
01:01	9400	10100	9700	9500	7500	3075	1050	775	1900	7025	8650	8725	20	70	89	92

B

Molasses added (ml)

Ratio: BW:RW	Start				End				Difference				Percent reduction			
pH	0	1	2	3	0	1	2	3	0	1	2	3				
05:01	6.21	6.23	6.14	6.09	5.98	5.95	5.73	5.65	0.23	0.28	0.41	0.44				
02:01	5.43	5.49	5.4		5.37	5.3	5.21		0.06	0.19	0.19					
01:01	5.04	4.99	4.98	4.97	5.03	4.96	4.93	4.9	0.01	0.03	0.05	0.07				
COD																
05:01	17650	18600	18250	17550	12400	14875	15250	12725	5250	3725	3000	4825	30	20	16	27
02:01	17400	17550	18550		8650	9650	9400		8750	7900	9150		50	45	49	
01:01	17700	19200	19750	20550	9200	9600	10050	9975	8500	9600	9700	10575	48	50	49	51
TSS																
05:01	6700	6600	6750	7250	2900	2950	3150	1900	3800	3650	3600	5350	57	55	53	74
02:01	8450	7550	8250		550	575	600		7900	6975	7650		93	92	93	
01:01	9400	10100	9700	9500	600	600	675	775	8800	9500	9025	8725	94	94	93	92

C

sludge added (ml)

Ratio: BW:RW	Start				End				Difference				Percent reduction			
pH	0	20	40	60	c	20	40	60	0	20	40	60				
5:1	6.49	6.41	6.36	6.3	6.3	6.13	6.03	5.92	0.19	0.28	0.33	0.38				
2:1	6	5.9	5.93		5.79	5.59	5.57		0.21	0.31	0.36					
1:1	5.37	5.4	5.43	5.45	5.17	5.12	5.1	5.07	0.2	0.28	0.33	0.38				
									0.2	0.29	0.34	0.38				
COD																
250:50	23250	26325	26225	27050	12900	13538	13250	9963	10350	12788	12975	17088	45	49	49	63
200:100	22425	23675	25700		8363	7688	7300		14063	15988	18400		63	68	72	
150:150	21425	23525	23975	24625	6850	7000	6688	6250	14575	16525	17288	18375	68	70	72	75
TSS																
250:50	7950	9300	10950	11700	6750	7600	7700	3100	1200	1700	3250	8600	15	18	30	74
200:100	9500	11350	11650		1675	1225	1325		7825	10125	10325		82	89	89	
150:150	11000	11700	12650	13800	725	900	825	725	10275	10800	11825	13075	93	92	93	95

Table 2: Raw data from batch tests (cont.)

D

Starch added

		Start				End				Difference				Percent reduction		
	pH	0	1	2	3	0	1	2	3	0	1	2	3			
	0	5.78	5.78	5.78	5.78	5.12	5.07	5.06	5.05	0.66	0.71	0.72	0.73			
	2	5.78	5.78	5.78		5.12	4.7	4.62		0.66	1.08	1.16				
	4	5.78	5.78	5.78	5.78	5.12	4.81	4.67	4.48	0.66	0.97	1.11	1.3			
	COD															
urea added (ml 5% soln)	0	11800	11800	11800	11800	10125			10150	1675			1650	14		
	2	11800	11800	11800		8475		9075		3325		2725		28		23
	4	11800	11800	11800	11800	7850			8850	3950			2950	33		
	TSS															
	0	3750	3750	3750	3750	1450	1900	1250	1200	2300	1850	2500	2550	61	49	67
	2	3750	3750	3750		550	450	450		3200	3300	3300		85	88	88
	4	3750	3750	3750	3750	550	475	500	475	3200	3275	3250	3275	85	87	87

E

Phosphorus added (ml 5% soln)

		Start				End				Difference				Percent reduction		
	pH	0	1	2		0	1	2		0	1	2				
	0	5.78	5.78	5.78		5.19	5.2	4.96		0.59	0.58	0.82	5.78			
	1	5.78	5.78	5.78		5.4	5.89	5.16		0.38	-0.11	0.62	5.78			
	2	5.78	5.78	5.78		5.56	5.44	5.26		0.22	0.34	0.52	5.78			
	COD															
urea added (ml 5% soln)	0	11800	11800	11800		8260	9084	7759		3540	2716	4041	11800	30	23	34
	0	11800	11800	11800		7166	3929	7812		4634	7871	3988	11800	39		34
	0	11800	11800	11800		8359	7363	7060		3441	4437	4740	11800	29	38	40
	TSS															
	0	3750	3750	3750		2027	1054	910.7		1723	2696	2839	3750	46	72	76
	0	3750	3750	3750		2000	2080	973.2		1750	1670	2777	3750	47		74
	0	3750	3750	3750		2009	1063	964.3		1741	2688	2786	3750	46	72	74

Table 3: Summary of batch test data.

A

Molasses

	COD	0	667	1000	1333	$mg.l^{-1}$
	5:1	36.54	32.12	30.41	27.07	**31.54**
Feed	2:1	37.36	36.61	30.59		**34.85**
	1:1	44.49	63.54	63.67	67.76	**59.87**
	Ratio	**39.46**	**44.09**	**41.56**	**47.41**	Avg
	TSS					
	5:1	50	48.48	49.26	51.38	**49.78**
Feed	2:1	15.68		44.55		**30.11**
Ratio	1:1	20.21	69.55	89.18	91.84	**67.7**
	Ratio	**28.63**	**59.02**	**60.99**	**71.61**	Avg
		5.98	5.95	5.73	5.65	**5.828**
	pH	5.37	5.3	5.21		**5.293**
		5.03	4.96	4.93	4.9	**4.955**
		5.46	**5.403**	**5.29**	**5.275**	Avg

B

Molasses 2

	COD	0	667	1000	1333	$mg.l^{-1}$
	5:1	29.75	20.03	16.44	27.49	**23.43**
Feed	2:1	50.29	45.01	49.33		**48.21**
	1:1	48.02	50	49.11	51.46	**49.65**
	Ratio	**42.68**	**38.35**	**38.29**	**39.48**	Avg
	TSS					
	5:1	56.72	55.3	53.33	73.79	**59.79**
Feed	2:1	93.49	92.38	92.73		**92.87**
Ratio	1:1	93.62	94.06	93.04	91.84	**93.14**
	Ratio	**81.27**	**80.58**	**79.7**	**82.82**	Avg
		6.92	6.7	6.5	6.4	**6.63**
	pH	6.05	5.9	6.2		**6.05**
		5.58	5.3	5	4.8	**5.17**
		6.183	**5.967**	**5.9**	**5.6**	Avg

C

Sludge

	COD	0	20	40	60	ml
	5:1	44.52	48.58	49.48	63.17	**51.43**
Feed	2:1	62.71	67.53	71.6		**67.28**
Ratio	1:1	68.03	70.24	72.11	74.62	**71.25**
	Ratio	**58.42**	**62.12**	**64.39**	**68.89**	Avg
	TSS					
	5:1	15.09	18.28	29.68	73.5	**34.14**
Feed	2:1	82.37	89.21	88.63		**86.73**
Ratio	1:1	93.41	92.31	93.48	94.75	**93.49**
	Ratio	**63.62**	**66.6**	**70.6**	**84.13**	Avg
		6.3	6.13	6.03	5.92	**6.095**
	pH	5.79	5.59	5.57		**5.65**
		5.17	5.12	5.1	5.07	**5.115**
		5.753	**5.613**	**5.567**	**5.495**	Avg

D

Starch

	COD	0	667	1000	1333	$mg.l^{-1}$
	0	14.19	15		13.98	**14.09**
urea	156	28.18	30	23.09		**25.64**
	311	33.47	32		25	**29.24**
	$mg.l^{-1}$	**25.28**	**25.67**	**23.09**	**19.49**	Avg
	TSS					
	0	61.33	49.33	66.67	68	**61.33**
urea	156	85.33	88	88		**87.11**
	311	85.33	87.33	86.67	87.33	**86.67**
	$mg.l^{-1}$	77.33	**74.89**	**80.44**	**77.67**	Avg
		5.12	5.07	5.06	5.05	**5.075**
	pH	5.12	4.7	4.62		**4.813**
		5.12	4.81	4.67	4.48	**4.77**
		5.12	**4.86**	**4.783**	**4.765**	Avg

E

Phosphorus

	COD	0	53	107	$mg.l^{-1}$
	0	30	23.02	34.25	**29.09**
urea	156	39.27		33.8	**36.54**
	311	29.16	37.6	40.17	**35.64**
	$mg.l^{-1}$	**32.81**	**30.31**	**36.07**	Avg
	TSS				
	0	45.95	71.9	75.71	**64.52**
urea	156	46.67		74.05	**60.36**
	311	46.43	71.67	74.29	**64.13**
	$mg.l^{-1}$	**46.35**	**71.79**	**74.68**	Avg
		5.31	5.32	5.08	**5.237**
	pH	5.52	6.01	5.28	**5.603**
		5.68	5.56	5.38	**5.54**
		5.503	**5.63**	**5.247**	Avg

7.4 Appendix 4: Results for Continuous Acidogenic reactor, Methanogenic reactor and Aerobic reactor.

Table 1: Raw data.

	Flow		COD					TSS					pH					VFA	Aciogenic
	l/h	sludge	Feed	Reactor	Effluent	Methanogenic	Aerobic	Feed	Reactor	Effluent	Methanogenic	Aerobic	Feed	Reactor	Effluent	Methanogenic	Aerobic	Feed	Effluent
	0.33	250	12575	11550	7925	3325	890	3434	3070	848	476	176	5.33	5.33	5.33	7.68	8.89		
	0.33	825	10825	10300	6025	2050	860	2558	2884	398	298	165	5.13	4.92	4.87	7.46	8.96		
	0.33	740	9750	10350	6700	2065	845	2196	2588	404	286	158	5.5	5.05	5.01	7.42	9.3		
	0.33	700	9500	10400	6150	1925	824	1904	2384	548	370	169	5.35	5.15	5.13	7.28	9.15		
	0.33	600	9835	10350	6250	1980	836	2532	2684	506	345	158	5.32	5.1	5.06	7.41	8.83		
Avg	**0.33**	**623**	**10497**	**10590**	**6610**	**2269**	**851**	**2524.8**	**2722**	**540.8**	**355**	**165.2**	**5.326**	**5.11**	**5.08**	**7.45**	**9.026**		
	0.1667	500	10264	13775	7528	2985	903	2563	2631	402	305	168	5.42	5.39	5.36	7.39	9.04	1027	1770
	0.1667	500	9862	6675	8053	3201	915	2025	2542	860	286	156	5.42	5.26	5.21	7.42	9.12	1183	1255
	0.1667	900	8590	7050	7428	2354	856	1980	2036	430	96	105	5.37	5.25	5.25	7.61	9.05		
	0.1667	400	7775	8325	6850	2032	862	1024	2070	444	236	158	5.7	5.13	5.45	7.49	8.96		
	0.1667	400	8125	6500	4375	1500	724	1426	1680	376	216	175	5.69	5.25	5.22	7.35	8.82	1183	1787
	0.1667	1000	10775	12575	7725	2423	862	1450	2658	362	274	142	5.72	5.28	5.3	7.7	8.96	1232	1605
	0.1667	1250	10875	11550		2153	875	1558	2720	330	276	132	5.41	5.09	5.07	7.6	9.03	1484	1583
	0.1667	1175	12525	12425	8775	3021	898	2684	3288	162	240	158	5.13	4.99	5	7.35	8.51	1415	1910
	0.1667	1200	15775	11650	7805	2512	869	3486	2054	302	106	120	5	4.84	4.87	7.69	8.78	1244	1752
	0.1667	810	8575	8850	7120	2136	836	1482	1948	226	138	134	4.85	4.74	4.76	7.87	8.98		
	0.1667	1000	11900	11575	8016	2865	896	2474	2294	718	268	136	6.06	5.25	5.2	7.22	9.06		
	0.1667		13500	15375				2550	3248		366	158	5.13	4.9		7.69	9.01	1553	2308
	0.1667	780	15500	13575	8425	2958	884	5226	2396	436	340	134	4.84	4.77	4.81	7.27	9.02	1362	2295
Avg	**0.1667**	**826.25**	**11080.1**	**10761.5**	**7463.64**	**2511.67**	**865**	**2302.15**	**2428.08**	**420.667**	**242.077**	**144.308**	**5.36462**	**5.08769**	**5.125**	**7.51154**	**8.94923**	**1298.11**	**1807.22**
	0.5	1900	12575	11850	8225			2042	2870	422	302	144	5.3	5.12	5.1	7.49	8.95	1840	2273
	0.5	2000	13800	14375	11075	2375	853	2574	3806	792	740	250	5.45	5.35	5.37	7.35	8.89	1510	1624
	0.5	1500	11900	12250	9568	3225	897	2476	3240	350	324	156	5.6	5.32	5.29	7.51	9.05		
	0.5	2000	14350	14501	10560	2689	864	2140	2950	482	308	148	5.42	5.38	5.35	7.66	9.04		
	0.5	1500	13520	11250	8500	2356	862	2340	3054	360	316	125	5.36	5.14	5.08	7.34	9.13		
Avg	**0.5**	**1780**	**13229**	**12845.2**	**9585.6**	**2661.25**	**869**	**2314.4**	**3184**	**481.2**	**398**	**164.6**	**5.426**	**5.262**	**5.238**	**7.47**	**9.012**	**1675**	**1948.5**
AVG	***0.279***	***1006.4***	***11441***	***11203***	***7780.7***	***2482.2***	***862.33***	***2356.4***	***2670.3***	***464.03***	***304.12***	***153.81***	***5.3699***	***5.1331***	***5.1413***	***7.4878***	***8.9814***	***1385.1***	***1839.8***
Max	***0.5***	***2000***	***15775***	***15375***	***11075***	***3325***	***915***	***5226***	***3806***	***860***	***740***	***250***	***6.06***	***5.39***	***5.45***	***7.87***	***9.3***	***1840***	***2308***
Min	***0.11***	***250***	***7775***	***6500***	***4375***	***1500***	***724***	***1024***	***1680***	***162***	***96***	***105***	***4.84***	***4.74***	***4.76***	***7.22***	***8.51***	***1027***	***1255***
Std	***0.1417***	***518.33***	***2202.2***	***2331.8***	***1490.8***	***474.72***	***37.349***	***813.18***	***493.84***	***176.01***	***122.78***	***26.373***	***0.2661***	***0.1842***	***0.1846***	***0.1596***	***0.146***	***224.87***	***310.5***

Table 2: COD and TSS reduction figures and COD loading rates.

	COD reduction						TSS reduction						Reactor COD loads				
	Acidognic		Methogenic		Aerobic		Acidogenic		Methogenic		Aerobic		Acid. load	Methanogenic load		Aerobic Load	
	reduction	%	reduction	%	reduction	%	reduction	%	reduction	%	reduction	%	kg/m3/day	mg COD/mg MLSS/d	kg/m3/day	mg COD/mg MLSS/d	kg/m3/d
	4650	37	4600	58	2435	73	2586	75	372	44	300	63	50	4.18	31	0.89	2.66
	4800	44	3975	66	1190	58	2160	84	100	25	133	45	43	3.18	24	0.55	1.64
	3050	31	4635	69	1220	59	1792	82	118	29	128	45	39	3.54	27	0.55	1.65
	3350	35	4225	69	1101	57	1356	71	178	32	201	54	38	3.25	24	0.51	1.54
	3585	36	4270	68	1144	58	2026	80	161	32	187	54	39	3.30	25	0.53	1.58
	2736	27	4543	60	2082	70	2161	84	97	24	137	45	14	1.32	10	0.80	2.39
	1809	18	4852	60	2286	71	1465	72	274	49	130	45	20	2.15	16	0.85	2.56
	1162	14	5074	68	1498	64	1550	78	290	67	35	25	17	1.98	15	0.63	1.88
	925	12	4818	70	1170	58	980	69	208	47	78	33	16	1.83	14	0.54	1.63
	3750	46	2875	66	776	52	1050	74	160	43	41	19	16	1.17	9	0.40	1.20
	3050	28	5302	69	1561	64	1088	75	88	24	132	48	22	2.06	15	0.65	1.94
					1278	59	1228	79	54	16	144	52	22			0.57	1.72
	3750	30	5754	66	2123	70	2322	87	122	34	82	34	25	2.34	18	0.81	2.42
	7970	51	5293	68	1643	65	3084	88	166	41	116	49	32	2.08	16	0.67	2.01
			4984	70	1300	61	1256	85	88	39	4	3		1.90	14	0.57	1.71
	3884	33	5151	64	1969	69	1756	71	450	63	132	49	24	2.14	16	0.76	2.29
	7075	46	5467	65	2074	70	3790	90	96	22	206	61	31	2.25	17	0.79	2.37
	4350	35					1620	79	120	28	158	52	75	6.58	49		
	2725	20	8700	79	1522	64	1982	77	152	26	190	43	83	8.86	66	0.63	1.90
	2332	20	6343	66	2328	72	2126	86	26	7	168	52	71	7.65	57	0.86	2.58
	3790	26	7871	75	1825	68	1658	77	174	36	160	52	86	8.45	63	0.72	2.15
	5020	37	6144	72	1494	63	1980	85	44	12	191	60	81	6.80	51	0.63	1.88
Max	***3688***	***31***	***5244***	***67***	***1620***	***64***	***1864***	***79***	***161***	***34***	***139***	***45***	***40***	***3.67***	***28***	***0.66***	***1.99***
Min	***7970***	***51***	***8700***	***79***	***2435***	***73***	***3790***	***90***	***450***	***67***	***300***	***63***	***86***	***8.86***	***66***	***0.89***	***2.66***
Avg	***925***	***12***	***2875***	***58***	***776***	***52***	***980***	***69***	***26***	***7***	***4***	***3***	***14***	***1.17***	***9***	***0.40***	***1.20***
Std dev	***1723***	***11***	***1300***	***5***	***472***	***6***	***679***	***6***	***105***	***15***	***65***	***14***	***25***	***2.44***	***18***	***0.13***	***0.40***