HIGH TEMPERATURE BIOLOGICAL TREATMENT OF FOUL EVAPORATOR CONDENSATE FOR REUSE

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Abstract

There is increasing interest in the treatment and reuse of the sewered portion of the evaporator condensate from kraft pulp mills. The treated evaporator condensate could be used in brown stock washing, recausticizing and bleaching, instead of clean water. In addition to reducing the contaminant load to the existing combined mill effluent treatment system, reducing the raw water requirements and potentially reducing the impact of discharging the treated condensate to the environment, reusing the condensate could also result in significant energy savings if the heat content of the evaporator condensate can be recovered. Also, some legislation proposes a number of incentives for treating and reusing the condensate as process water.

Methanol and reduced sulphur compounds (RSC) were identified as the primary contaminants of concern contained in evaporator condensate. These contaminants are of concern primarily because they are hazardous air pollutants (HAP) and/or foul odorous compounds. Reusing evaporator condensate in a pulp mill without treatment could result in the subsequent emission of HAP and odorous compounds and generate unpleasant or even hazardous working conditions for mill staff. Some trace organic contaminants contained in evaporator condensate are also of concern primarily because they could disrupt the pulping process and impact pulp quality. A number of conventional technologies have been considered for the treatment of evaporator condensate for reuse. However, the relatively poor treatment efficiencies and/or high costs associated with these technologies provided incentives to investigate and develop a better treatment technology. A high temperature membrane bioreactor (MBR) was selected as the most promising novel technology for the treatment of evaporator condensate for reuse.

A preliminary study indicated that the biological removal of methanol from synthetic evaporator condensate using a high temperature MBR was feasible. The results suggested that the specific methanol utilization coefficient was higher during high

temperature biological treatment using an MBR, than in a conventional biological treatment system.

However, simultaneous biological removal of methanol and RSC from synthetic condensate using a high temperature MBR was not feasible. A low operating pH was required for biological oxidation of RSC to occur at elevated temperatures. In addition, biological removal of methanol was significantly inhibited at the pH required for biological RSC removal to occur. Therefore, a two stage system, with the first stage operating at an acidic pH and the second stage operating at a neutral pH, would be required. This would add significantly to the cost of a biological system to treat evaporator condensate for reuse. Even at an optimal pH for the growth of sulphur-oxidizing microorganisms, stripping due to the aeration system accounted for approximately 50 % of the RSC removed from the MBR. The results also indicated that the stability of a mixed microbial culture at a low pH is questionable. For these reasons, the biological oxidation of RSC in a high temperature MBR was not considered to be feasible and simultaneous biological removal of methanol and RSC was not further investigated.

Further investigations revealed that it was possible to biologically remove methanol from synthetic evaporator condensate using a high temperature MBR, over the entire expected range of temperatures for evaporator condensate (55 to 70 °C). However, the operating temperature exerted a significant impact on methanol removal kinetics. A maximum specific methanol utilization coefficient and a maximum specific growth coefficient of approximately 0.84 ± 0.08 /day and 0.11 ± 0.011 /day, respectively, were observed at an operating temperature of 60 °C. Above 60 °C, both the specific methanol utilization coefficient and the specific growth coefficient declined sharply, suggesting that at high operating temperatures, the inactivating effect of temperature on the growth-limiting enzyme must be considered. A relatively simple model was proposed and used to accurately estimate the effect of high temperatures on methanol removal kinetics in an MBR over the temperature range investigated. Based on the model, the optimal operating temperature for the biological removal of methanol by a mixed microbial

culture was determined to be approximately 60 °C. These results indicated that it is not only possible to operate an MBR at high temperatures, but also that a higher specific methanol utilization coefficient can be achieved at a higher operating temperature. However, care may need to be taken not to exceed the critical operating temperature of 60 °C.

The operating temperature was also observed to have a significant effect on the observed microbial growth yield in the MBR. At increasing operating temperatures, a larger fraction of the methanol consumed was converted to energy, reducing the observed growth yield. These results indicate that at high temperatures, less excess sludge may be produced, potentially resulting in lower waste sludge handling and disposal costs.

The specific methanol utilization coefficient measured during the treatment of real evaporator condensate was lower than that observed when treating synthetic evaporator condensate. The difference was not due to a direct toxic effect from compounds present in the real evaporator condensate matrix. The reduction was attributed to a shift in the composition of the microbial community present in the MBR. The shift resulted from competition between methylotrophic and partial-methylotrophic microorganisms for the available methanol. Microorganisms that were not capable of growth on methanol as sole substrate, but were capable of consuming methanol in the presence of other organic substrates, were defined as partial-methylotrophic microorganisms. The partial-methylotrophic microorganisms exhibited a lower specific methanol utilization coefficient (0.29/day) than the methylotrophic microorganisms (0.84/day), resulting in a lower overall specific methanol utilization coefficient for the mixed microbial culture of 0.59 ± 0.11 /day. Nonetheless, the specific methanol utilization coefficient observed at 60 °C was still more than 30 % higher than previously reported values from other studies of biological treatment of condensate at much lower temperatures.

High temperature biological treatment using an MBR also successfully removed the non-methanolic contaminants of concern contained in evaporator condensate. Over 99 % of the RSC contained in the evaporator condensate was removed during high temperature

treatment using an MBR. The concentrations of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl sulphide in the evaporator condensate werereduced to below detection limits (approximately 0.4 mg/L) during high temperature operation using an MBR. Approximately 93 % of the organic compounds, measured as TOC, contained in the evaporator condensate could be removed. The concentration of TOC in the evaporator condensate was reduced from 504 ± 137 mg/L to 52 ± 3.6 mg/L. Over 78 % of the reduction in TOC was due to the removal of methanol.

Based on assumed removal efficiencies of 99, 90 and 99 % for methanol, TOC and RSC (as hydrogen sulphide and methyl mercaptan), respectively, as well as the characteristics of the evaporator condensate from a local kraft pulp mill, a conceptual design for a full-scale, high temperature MBR to treat an evaporator condensate for reuse was developed. Capital and operating costs were estimated and compared to the costs for a steam stripping system. Depending on the type of ultrafiltration membranes used in the MBR design, the capital cost for the MBR system was 40 to 50 % less than the capital cost of a steam stripping system capable of achieving comparable contaminant removal efficiencies. The operating costs for the MBR system were also approximately 50 % less than the operating costs for a steam stripping system. Therefore, high temperature biological treatment is not only technically feasible, but is also appears to be economically more attractive than the currently favored treatment technology (i.e. steam stripping).

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Nomenclature

μ: Specific growth coefficient (/day)

θ: Temperature activation coefficient (-)

θ': Temperature inactivation coefficient (-)

μ_D: Specific growth coefficient at operating temperature T'_D (/day)

θ_{MeOH}: Hydraulic retention time required to remove methanol (hours)

θ_{TOC}: Hydraulic retention time required to remove TOC (hours)

μ_T: Specific growth coefficient at operating temperature T (/day)

$\mu_{T'}$: Specific growth coefficient at operating temperature T' (/day)

[H+]: Concentration of hydrogen ions at a given pH (mg/L)

a: Constant (-)

A: Arrhenius activation constant (/day)

B: Arrhenuis inactivation constant (-)

B': Inactivation constant (-)

C_E: Concentration of methanol in treated effluent (mg/L)

C_{MeOH}: Concentration of methanol in the MBR (mg/L)

C_O: Initial concentration of methanol (mg/L)

C_{RSC}: Concentration of RSC in the MBR (mg/L)

E: Arrhenius activation energy for growth-limiting reaction (J/mole)

E': Arrhenius inactivation energy for the growth-limiting reaction (J/mole)

f_A: Active fraction of growth-limiting enzymes (-)

f_I: Inactive fraction of growth-limiting enzymes (-)

HAP: Hazardous air pollutant

HRT: Hydraulic retention time (hours)

K_1: Dissociation constant (mg/L)

K_2: Dissociation constant (mg/L)

$K_{B\text{-}MeOH}$: Zero order coefficient for the biological removal of methanol (mg/L•minute)

$K_{B\text{-}RSC}$: First order coefficient for the biological removal of RSC (/minute)

Ki_{MeOH}: Half inhibition concentration for methanol (mg/L)

Ki_{RSC}: Half inhibition concentration for RSC (mg/L)

K_{MeOH}: Zero order coefficient for the removal of methanol (mg/L•minute)

Ko_{pH}: Maximum biological removal coefficient at the optimal pH (/minute)

K_{pH}: Biological removal coefficient at a given pH (/minute)

K_{RSC}: Biological RSC removal coefficient (/minute)

Ks_{MeOH}: Half saturation concentration for methanol (mg/L)

Ks_{RSC}: Half saturation concentration for RSC (mg/L)

$K_{STRIP\text{-}MeOH}$: First order coefficient for the stripping of methanol (/minute)

$K_{STRIP\text{-}RSC}$: First order coefficient for the stripping of RSC (/minute)

$K_{STRIP\text{-}TOC}$: First order coefficient for the stripping of TOC (/minute)

$K_{T\text{-}RSC}$: First order coefficient for the total removal of RSC (/minute)

MBR: Membrane bioreactor

MLVSS: Mixed liquor volatile suspended solids (mg/L)

n: Reaction order not limited to integers (-)

R: Universal gas constant (8.314 J/K.mole)

$R_{B\text{-}MeOH}$: Rate of biological methanol removal (mg/L•minute)

R_G: Rate of microbial growth (mg/L•day)

$R_{RSC\text{-}N}$: Rate of RSC removal at a neutral pH (mg/L•minute)

RSC: Reduced sulphur compounds

$R_{S\text{-}MeOH}$: Rate of methanol removal due to stripping (mg/L•minute)

$R_{T\text{-}MeOH}$: Total rate of methanol removal (mg/L•minute)

$R_{T\text{-}RSC}$: Total rate of RSC removal (mg/L•minute)

S : Concentration of the multi-component substrate (mg/L as TOC)

S_E: Concentration of TOC in treated effluent (mg/L as TOC)

S_N: Non-degradable component of the multi-component substrate (mg/L as TOC)

S_{NS}: Non-volatile component of the multi-component substrate (mg/L as TOC)

S_O: Initial concentration of multi-component substrate (mg/L as TOC)

SRT: Sludge retention time (days)

T: Absolute operating temperature (K)

T': Operating temperature (^oC)

T'_D: Datum operating temperature (^oC)

TOC: Total Organic Carbon (mg/L)

U_M: Specific methanol utilization coefficient for methylotrophic microorganisms (/day)

U_{MeOH}: Specific methanol utilization coefficient (/day)

U_{N-M}: Specific methanol utilization coefficient for non-methylotrophic microorganisms (/day)

U_{RSC}: Specific RSC utilization coefficient (/day)

U_{TOC}: Specific TOC utilization coefficient (/day)

U_{TOC-72}: First order specific TOC utilization coefficient for Equation 7.2 (L/mg•day)

U_{TOC-73}: First order specific TOC utilization coefficient for Equation 7.3 (/day)

U_{TOC-74}: First order specific TOC utilization coefficient for Equation 7.4 (/day)

U_{TOC-75}: n^{th} order specific TOC utilization coefficient for Equation 7.5 (/day)

U_{TOC-76}: First order specific TOC utilization coefficient for Equation 7.6 (day)

X: Concentration of MLVSS in the MBR (mg/L)

X_i: Concentration of MLVSS for specific group of methanol consuming microorganisms (mg/L)

X_{M_f}: Concentration of MLVSS for methylotrophic microorganisms (mg/L)

X_{To_f}: Concentration of MLVSS for both groups of methanol consuming microorganisms for specific fraction of real evaporator condensate(mg/L)

X_{N-M_f}: Concentration of MLVSS for non-methylotrophic microorganisms (mg/L)

Y: Observed growth yield (mg biomass produced/mg methanol consumed)

Y_{i_f}: Observed growth yield for specific group of methanol-consuming microorganisms for specific fraction of real evaporator condensate (mg/mg)

Y_{M_f}: Observed growth yield methylotrophic microorganisms for specific fraction of real evaporator condensate (mg/mg)

Y_{To_f}: Observed growth yield for both groups of methanol consuming microorganisms for specific fraction of real evaporator condensate(mg/mg)

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Preface

Some of the results contained in this thesis have been published in conference proceedings and peer reviewed journals. Below is a list of the currently published material.

1. Bérubé P.R. and Hall E.R. (2000) Effect of temperature on methanol removal kinetics from synthetic kraft pulp mill condensates using a membrane bioreactor, Water Research (in press).

2. Bérubé P. R. and Hall E. R. (2000) Fate and removal kinetics of contaminants contained in evaporator condensate during treatment of reuse using a high temperature membrane bioreactor, Journal of Pulp and Paper Science (in press) (Also 86th PAPTAC Annual Meeting, Montreal, February 2000, B67-B72).

3. Bérubé P. R. and Hall E. R. (2000) Treatment of recovery cycle condensate using a high temperature membrane bioreactor: Determination of maximum operating temperature and system costs, Pulp and Paper Canada, 101(3), 54-58, (Also Proceedings TAPPI Environmental Conference, April 1999, 769-782 and PAPTAC Pacific and Western Branches Conference, May 1999).

   Note: This paper has been awarded the 1999 I.H. Weldon Medal by the Pulp and Paper Technical Association of Canada for the best paper presented at any Association meeting.

4. Bérubé P. R. and Hall E. R. (1999a) Effects of kraft evaporator condensate matrix on methanol removal in a high temperature membrane bioreactor, Water Science and Technology, 40 (11/12), 327-335 (Also, Proceedings 6th IAWQ Symposium on Forest Industry Wastewaters, June 1999, 345-353).

5. Bérubé P.R., Parkinson P.D. and Hall E.R. (1999b) Measurement of reduced sulphur compounds in aqueous matrices by direct injection into a gas chromatograph with flame photometric detector, Journal of Chromatography A, 830, 485-489.

6. Bérubé P. R. and Hall E. R. (1999c) Determination of the optimal operating temperature for the biological removal of methanol from synthetic kraft mill evaporator condensate, Proceedings Sustainable Forest Management Conference, Science and Practice: Sustaining the Boreal Forest, February 1999, 263-268.

In addition, a number of articles have been submitted for publication or are under preparation as listed below.

1. Bérubé P. R., Hall E. R., Biological removal of reduced sulphur compounds from synthetic evaporator condensate during treatment using a high temperature membrane bioreactor (to be presented at the 3rd Western Canadian Symposium on Water Pollution Research, Vancouver, May 8-9, 2000).

2. Bérubé P.R. and Hall E.R., Cost comparaison between a high temperature membrane bioreactor and a steam stripper for the treatment of foul evaporator condensate for reuse (in preparation).

Chapter 1 – Introduction

1.1 Problem Definition

Tighter regulatory requirements and public interest in "environmentally friendly" pulp and paper products have encouraged the Pulp and Paper Industry to refine its wastewater treatment practices (Mannisto et al., 1996; NCASI, 1998). As an alternative to conventional end-of-pipe wastewater treatment, some mills are considering closing up selected process water systems to reuse the wastewater as process water (Bérubé and Hall, 1996). Reusing the wastewater can reduce the contaminant load to the existing combined mill effluent treatment system, reduce the raw water requirements, and potentially reduce the impact of discharging treated wastewater to the environment (Vora and Venkataraman, 1995; NCASI, 1998; Blackwell et al., 1979).

Under current operating conditions, kraft pulp mills typically reuse a portion of the cleaner fraction of the evaporator condensate along with clean water as process water in brown stock washing and recausticizing (NCASI, 1998). However, the portion of clean evaporator condensate that can be reused is typically limited to approximately 30 to 50 % (Mattsson, 1996; personal communication, Taylor J., Western Pulp Limited Partnership, Squamish, Canada). Reusing a larger portion could result in ambient air quality problems because of the subsequent release of hazardous air pollutants (HAP) and foul odorous compounds contained in the clean condensate (Venkatesh et al., 1997; Jain, 1996; Jett, 1995; NCASI, 1994c-g) Such emissions can cause unpleasant or even hazardous working conditions for mill staff (ACGIH, 1999). The non-reused portion of the clean evaporator condensate is typically sewered and then treated in a combined mill effluent treatment system before being discharged to the environment. The foul fraction of the evaporator condensate, which contains even higher concentrations of HAP and foul odorous compounds, is also sewered, treated and discharged to the environment. Some mills steam strip the foul evaporator condensate before sewering it to minimize potential

ambient air quality problems that could occur during subsequent treatment in the combined mill effluent treatment system (NCASI, 1994a).

There is increasing interest in the treatment and reuse of the sewered portion of the evaporator condensate (Barton et al., 1996; Vora and Verkataraman, 1995). The treated evaporator condensate could be reused in brown stock washing, recausticizing and bleaching instead of clean water (Sebbas, 1987; Pekkanen and Kiiskilä, 1996). The process water demand in a kraft pulp mill is typically high enough for all of the treated evaporator condensate to be reused for brown stock washing alone (Sebbas, 1987). In addition to reducing the contaminant load to the existing combined mill effluent treatment system, reducing the clean water requirements and potentially reducing the impact of discharging the treated condensate to the environment, reusing the condensate could also result in significant energy savings if the heat content of the evaporator condensate can be recovered (Sebbas, 1987; Durham, 1991). Also, some legislation proposes a number of incentives for treating and reusing the condensate as process water (Vice and Carroll, 1998). The ability to treat the foul evaporator condensate for reuse would be a significant step towards the ultimate goal of a zero effluent mill.

A number of conventional technologies exist that could be used to treat the condensate for reuse. However, the relatively poor treatment efficiencies and/or the high costs associated with these conventional systems provided incentives to investigate and develop better treatment technologies for evaporator condensate treatment for reuse.

1.2 Objectives of the Study

A research program was initiated to identify and investigate a novel technology that would be suited for the treatment of evaporator condensate for reuse. As discussed in Section 2.3.5, high temperature aerobic biological treatment using a membrane bioreactor (MBR) was selected as the most promising novel technology for the treatment of

evaporator condensate for reuse. However, very little was known about the biological treatment of condensate, especially at elevated temperatures.

The overall objective of the present study was to improve our understanding of the physical, chemical and biological processes that occur during the high temperature biological treatment of evaporator condensate using an MBR. A better understanding of these processes is necessary to properly evaluate, design and operate a high temperature MBR for the treatment of evaporator condensate for reuse. The specific objectives are as listed below.

1. Determine the feasibility of biologically removing the main contaminants of concern present in evaporator condensate using a high temperature MBR. As discussed in Section 2.2, methanol, RSC and trace organic compounds were identified as the main contaminants of concern contained in evaporator condensate.

2. Identify the effects of operating an MBR at temperatures that are typical of that for an evaporator condensate stream, on the fate and removal kinetics of the main contaminants of concern during biological treatment. As discussed in Section 2.1, the temperature of an evaporator condensate stream is relatively high, ranging from 55 to 70 °C. It was desirable to operate the biological treatment system in this temperature range to minimize cooling requirements and maximize the recovery of the heat content of the evaporator condensate.

3. Identify the effects of the contaminants present in the condensate matrix on the biological treatment of evaporator condensate. As discussed in Section 2.1, evaporator condensate contains numerous contaminants, many of which can inhibit microbial activity in the treatment process.

4. Identify the fate and removal kinetics of the main contaminants of concern present in evaporator condensate during biological treatment using a high temperature MBR.

5. Determine the economical feasibility of using a high temperature MBR to treat evaporator condensate for reuse.

1.3 Study Outline

Based on the literature review, presented in Chapter 2, high temperature aerobic biological treatment using an MBR was selected for the treatment of kraft pulp mill evaporator condensate for reuse. High temperature aerobic biological treatment using an MBR appeared to be more efficient and less costly than conventional treatment systems. However, as outlined in Section 2.3.4, there was no information available regarding the aerobic biological treatment of evaporator condensate at high temperatures and only limited information available regarding the aerobic biological removal of contaminants such as methanol and RSC, at high temperatures.

The overall objective of the present study was to improve our understanding of the physical, chemical and biological processes that occur during the high temperature biological treatment of evaporator condensate using an MBR. To address this objective, a series of experiments were designed and conducted as outlined below (also summarized in Table 3.1).

The first experiment determined the feasibility of biologically removing methanol and RSC using an aerobic high temperature MBR. The bench scale MBR used for this, and subsequent experiments, is described in Chapter 3. The results from this experiment are presented in Chapter 4. The preliminary results from the first experiment suggested that a high temperature aerobic biological treatment system can be more efficient than a

conventional aerobic biological treatment system operating at a much lower temperature for the removal of methanol from evaporator condensate.

The second experiment investigated the effect of high temperature operation on the aerobic biological removal of methanol from evaporator condensate. The results are presented in Chapter 5. Based on the results from the second experiment, the optimal operating temperature for the aerobic biological treatment of evaporator condensate for reuse was determined. Again the results suggested that high temperature aerobic biological treatment can be more efficient than a conventional aerobic biological treatment system operated at a much lower temperature.

The first two experiments were conducted using synthetic evaporator condensate. Real evaporator condensate contains numerous trace compounds, many of which are known to inhibit microbial activity in a biological treatment system. The absence of these trace compounds in synthetic evaporator condensate could explain the higher treatment efficiency observed during the first two experiments compared to the treatment efficiency reported by others when treating real evaporator condensate using conventional aerobic biological treatment systems operating at much lower temperatures. The third experiment investigated the effect of the contaminants present in the condensate matrix on the removal of methanol from evaporator condensate using an aerobic high temperature MBR. The results are presented in Chapter 6.

The first three experiments investigated the biological removal of methanol from evaporator condensate during high temperature aerobic biological treatment. The fourth experiment investigated the fate and removal kinetics, of the non-methanolic contaminants of concern present in evaporator condensate, during high temperature aerobic biological treatment. The results are presented in Chapter 7.

In addition to the experimental investigations, the present study also investigated the economic feasibility of using an aerobic high temperature MBR for the treatment of evaporator condensate for reuse. Based on the information collected during the four

experiments, a conceptual design of a full scale MBR was performed and the capital and operating costs were estimated. The economic feasibility was assessed by comparing the costs for a high temperature MBR to the costs for a steam stripping system for the treatment of evaporator condensate for reuse. Steam stripping is considered by many to be the best currently available conventional technology for the treatment of evaporator condensate. The results are presented in Chapter 8.

The final part of the present study summarizes the conclusions reached during the different experiments conducted throughout this study. The implications of these conclusions to environmental process engineering are discussed. Recommendations for further research are also presented. The conclusions, significance of the results to environmental process engineering and recommendations for further studies are presented in Chapter 9.

Chapter 2 – Condensate Treatment for Reuse

2.1 Characteristics of Evaporator Condensate

In the kraft pulping process, chemicals (sodium sulphate and sodium hydroxide) are added to wood furnish to convert the lignin, which binds the individual wood fibers together, into soluble products. The soluble products formed during the pulping process (spent cooking liquor) are subsequently rinsed from the individual wood fibers (pulp). Following the pulping process, the pulp is further processed into various paper products. The spent cooking liquor, referred to as weak black liquor, contains all of the chemicals initially added to the raw wood furnish during the pulping process, as well as a number of other compounds formed during the pulping process. The chemicals initially added to the wood furnish are recovered and reused. The first step in the recovery process is the concentration of the weak black liquor by evaporation. The concentrated black liquor is then further processed to complete the recovery of the pulping chemicals. The material that is evaporated during the thickening process is condensed. This condensed material is commonly referred to as the evaporator condensate. A comprehensive review of the kraft pulping process is presented by Smook (1992).

In addition to water, a number of compounds are volatilized from the black liquor during evaporation. Over 60 compounds have been identified to be present in evaporator condensate (Table 2.1). These compounds originate either from the wood furnish or are produced during the pulping process. As expected, most of the compounds listed in Table 2.1 are volatile or semi-volatile. However, some non-volatile compounds, such as resin acids, can also be found in the evaporator condensate. These non-volatile compounds are present in the evaporator condensate as a result of physical entrainment of weak black liquor from the evaporators to the condensers (Blackwell et al., 1979).

Table 2.1

Compounds Typically Found in Evaporator Condensate

Alcohols	α-terpinene	m-cresol
Methanol	Limonene	Vanillin
Ethanol	β-phellandrene	Acetovanillone
1-propanol	γ-terpinene	Dihydroxy Acetophenone
2-propanol	Terpinolene	4-dihydroxy-5-methoxy acetophenone
Butanol	Fenchone	**Acids**
2-methyl-1-propanol	Linalool	Resin acids
4-(p-tolyl)-1-pentanol	Fenchyl alcohol	Fatty acids
Ketones	Terpene-4-ol	Formic acid
Acetone	α-terineol	Acetic acid
3-methyl-2-butanone	Cineole	Lactic acid
2-butanone (MEK)	Dipentene	**Aldehydes**
3-pentanone	**Reduced Sulphur Compounds**	Acetaldehyde
4-methyl-2-pentanone MIBK)	Hydrogen sulphide	**Dissolved gases**
2-heptanone	Methyl mercaptan	Methane
Terpenes	Dimethyl sulphide	Ethene
α-pinene	Dimethyl Disulphide	Ethane
β-pinene	**Phenolics**	Propene
Camphene	Guaiacol	Propane
Mycrene	Syringol	Carbon dioxide
Δ-3-carene	Phenol	Ammonia
p-cymene	o-cresol	**Others**
α-phellandrene	Dimethyl Trisulphide	2-methyl furan
	Thiophene	Toluene
	p-cresol	$C_{10}H_{24}$ to $C_{16}H_{34}$

(Adapted from Blackwell et al., 1979; Barton et al., 1998)

Methanol and reduced sulphur compounds (RSC) are the most abundant compounds found in the evaporator condensate (Blackwell et al., 1979). Methanol often accounts for up to 95% of the organic material contained in the evaporator condensate (Blackwell et al., 1979). Methanol is believed to originate from the alkaline hydrolysis of 4-o-methyl glucuronic acid residues in hemicellulose during the pulping process (Wilson and Hrutfiord, 1971; Sarkanen et al., 1970). The most abundant RSC contained in the evaporator condensate are hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH),

dimethyl sulphide ($(CH_3)_2S$ - DMS) and dimethyl disulphide ($(CH_3)_2S_2$ - DMDS). Total reduced sulphur (TRS) is also commonly used to refer to RSC. However, TRS implies that all RSC are grouped together into one multi-component parameter. In the present study the individual RSC are considered separately. Consequently, RSC was used during the present study to refer to these compounds. Hydrogen sulphide is formed from the dissociation of sodium sulphide used in the pulping liquor. Methyl mercaptan, as well as DMS, are formed during the breakdown of lignin into methoxy groups during pulping (McKean et al., 1965; Douglass and Price, 1966). DMDS is formed from methyl mercaptan by oxidation when black liquor comes into contact with air after the pulping cycle is complete (McKean et al., 1965). These four RSC are responsible for most of the odor problems associated with bleached kraft pulp and paper mills (Sarkanen et al., 1970). Ethanol, acetone, acetaldehyde, methyl ethyl ketone and terpenes make up the bulk of the remaining contaminants typically present in the evaporator condensate. The concentrations of these latter contaminants are typically one to two orders of magnitude lower than that for methanol or the RSC (Blackwell et al., 1979).

The evaporator condensate is typically segregated into a foul and a cleaner fraction. The foul fraction of the evaporator condensate is formed from the initial evaporation of weak black liquor. This foul fraction typically contains approximately 80% and 98% of the total amount of methanol and RSC, respectively, generated in the recovery cycle, and typically accounts for less than 40% of the total evaporator condensate flow (Blackwell et al., 1979). In newer mills, the foul fraction of the evaporator condensate flow can be as low as 5 to 10 % of the total evaporator condensate flow (Burgess, 1991; Sebbas, 1987). The clean fraction of the evaporator condensate is formed from the subsequent evaporation of the partially thickened black liquor. This cleaner fraction contains fewer volatile contaminants and is typically clean enough to be reused without treatment (Blackwell et al., 1979). Under current operating practices, kraft pulp mills typically reuse approximately 30 to 50 % of the clean fraction of the evaporator condensate without treatment in brownstock washing and recausticizing (Mattsson, 1996; Personal communication, Taylor J., Western Pulp Limited Partnership, Squamish, Canada). The non-reused portion is sewered and then treated in a combined mill effluent treatment

system before being discharged to the environment. The foul fraction of the evaporator condensate is too contaminated to be reused without treatment. Under current operating practices, the entire foul fraction of the evaporator condensate is sewered, treated and then discharged to the environment.

The exact composition and concentration of the compounds contained in evaporator condensates are functions of a number of parameters, including the wood species pulped, the pulping process used, the evaporator and condenser configuration, the use of a turpentine recovery system and other operating parameters. The effect of these parameters on the characteristics of evaporator condensate is discussed in Carter and Tench (1974), NCASI (1994b), Burgess (1991), Sebbas (1987), Blackwell et al. (1979), Wilson and Hrutfiord (1971) , Sarkanen et al. (1970) and McKean et al. (1965). Of the compounds listed in Table 2.1, methanol, RSC, other non-methanolic organic compounds and suspended solids were identified as the contaminants of concern (Section 2.2). Typical values for the concentrations of these contaminants in the foul fraction of evaporator condensate are presented in Table 2.2.

Table 2.2

Typical Characteristics of the Foul Fraction of Evaporator Condensate

Parameter	Typical Value
Methanol (mg/L)	180-1200
Reduced Sulphur Compounds	
Hydrogen Sulphide (mg/L)	1-240
Methyl Mercaptan (mg/L)	1-410
Dimethyl Sulphide (mg/L)	1-15
Dimethyl Disulphide (mg/L)	1-50
Total Organic Content (mg/L as BOD)	450-2500
Suspended Solids (mg/L)	30-70

(Typical Values from Blackwell et al., 1979)

The temperature of evaporator condensate typically ranges from 55 to 70 °C and the pH typically varies from 7.5 to 8.5 (Zuncich et al., 1993; Sebbas, 1987; Blackwell et al., 1979). However, the pH can be much higher when weak black liquor is physically

entrained into the condensers during evaporation. The total evaporator condensate flow typically ranges from 4 to 10 m^3/admt (air dried metric tonne), although the flow can be significantly less in newer mills (Sebbas, 1987; Blackwell et al., 1979).

2.2 Treatment Requirements for the Reuse of the Foul Fraction of Evaporator Condensate

To be reused as process water, the foul fraction of the evaporator condensate must be treated. For the remainder of this thesis, the foul fraction of the evaporator condensate will be referred to as evaporator condensate. Of particular concern are the hazardous air pollutants (HAP) and foul odorous compounds contained in the evaporator condensate. These contaminants could volatilize to the atmosphere, potentially resulting in unpleasant or even hazardous working conditions for mill staff (Jain, 1996; Venkatesh et al., 1997; Jett, 1995; NCASI, 1994c-g). In addition, the presence of other trace organic compounds or particulate matter could disrupt pulping processes (Sebbas, 1987; Annola et al., 1995; Niemela et al., 1999)

2.2.1 Regulating the Emission of HAP and Foul Odorous Compounds

The main HAP and foul odorous compounds present in the evaporator condensate are methanol, hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide. Methanol is classified as a HAP by the United States Environmental Protection Agency (Clean Air Act, 1990). Although methanol itself is not toxic to humans, the metabolic product of inhaled methanol is. Formic acid, formed during the metabolism of methanol, can lead to metabolic acidosis and can impact the visual system (Medinsky et al., 1997). This can lead to headaches, dizziness, blurred vision, nausea, vomiting, severe abdominal pain, difficulty breathing, blindness and even death (Medinsky et al., 1997). Reported minimum inhibitory concentrations for ambient methanol range from 200 to 375 ppm for humans (Shusterman et al., 1993). At these

concentrations, high incidences of headaches are commonly reported (Shusterman et al., 1993).

The RSC (hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide) are foul odorous compounds with extremely low odor thresholds which can cause unpleasant conditions for mill staff. Hydrogen sulphide and methyl mercaptan, which are characterized by a foul rotting egg odor and rotting cabbage odor, respectively, are detectable at very low concentrations. Their respective detection thresholds are approximately 0.001 ppm and 0.0001 ppm (Verschueren, 1996). The odors associated with dimethyl sulphide and dimethyl disulphide are not as foul and their detection thresholds are 1 to 2 orders of magnitude higher than those of hydrogen sulphide and methyl mercaptan (Verschueren, 1996).

The RSC are not only of concern because of their foul odor, but also because of their toxicological effects on humans. The toxicological effects of all four RSC are similar, that is, they affect the respiratory chain in all aerobic cell mitochondra (i.e broad spectrum toxicant) (Tatum, 1995). Some symptoms of exposure to RSC include eye irritations (tearing, photophobia), headaches, sore throat, nausea, vomiting, chest pains, respiratory failure and even death (Tatum, 1995). Hydrogen sulphide is the most toxic of the RSC contained in condensate, followed closely by methyl mercaptan (Kangas et al., 1984). Dimethyl sulphide and dimethyl sulphide are reported to be much less toxic than hydrogen sulphide (Kangas et al., 1984). Due to their extremely foul odors at low detection thresholds, exposure to lower concentrations of RSC can also cause a number of physiological and psychological responses in humans (Reifenstein et. al., 1995; Tatum, 1995). Some of the physiological and psychological responses to the exposure of low concentrations of these foul smelling compounds are visual fatigue, nausea, vomiting, headaches, insomnia, lethargy, depression, irritability, amnesia, disequilibrium and anorexia. Reported minimum inhibitory concentrations for ambient hydrogen sulphide range from 5 to 10 ppm (Reiffenstein et. al., 1995; Tatum, 1995). At these concentrations, high incidences of eye irritations and headaches are commonly reported.

In addition to methanol and RSC, relatively high concentrations of ethanol, acetaldehyde, acetone, methyl ethyl ketone (MEK), terpenes and phenolics can be present in evaporator condensate (Blackwell et al., 1979; Barton et al., 1998). Of these, acetaldehyde, acetone, MEK and terpenes are considered to be HAP (Clean Air Act, 1990). However, because of their presence at relatively low concentrations in evaporator condensate, the ambient air concentrations of these compounds are not expected to be significant.

A number of regulations exist to ensure safe ambient air quality for pulp and paper mill staff. In North America, these regulations fall into two categories: ambient air quality regulations or liquid phase regulations.

Ambient Air Quality Regulations

Ambient air quality regulations set limits for which no, or minimal, effects from exposure to HAP or foul odorous compounds can be detected. For many jurisdictions, including Canada and the United States, the ambient air quality regulations are based on standards recommended by the American Conference of Government and Industrial Hygienists (ACGIH, 1999). The ACGIH ambient air quality standards that are of importance to the pulp and paper industry are listed in Table 2.3. Methyl mercaptan has a much lower acceptable limit because it is detectable at much lower concentrations.

Table 2.3

ACGIH Ambient Air Quality Standards for Kraft Pulp Mills

Volatile Contaminant	**ACGIH Standard** (ppm)
Methanol	200
Hydrogen sulphide	10
Methyl Mercaptan	0.5

(based on an 8 hour per day and 5 days per week exposure)

Jappinen et al. (1993), Kangas et al. (1993) and Leech and Chung (1982) investigated the ambient air quality, with respect to RSC, at a number of kraft pulp mills. The ACGIH air quality standards for hydrogen sulphide were generally met. However, the air quality standards for methyl mercaptan were often exceeded in all areas and for all mills investigated. The reported ambient air concentrations for hydrogen sulphide typically ranged from <0.05 to 8.0 ppm with a reported maximum of 20 ppm. Ambient air concentrations for methyl mercaptan ranged from 0.01 to 15 ppm. There are no ACGIH ambient air quality standards for dimethyl sulphide and dimethyl disulphide, since these RSC are much less toxic and their odors are detectable at much higher odor thresholds than hydrogen sulphide and methyl mercaptan. The release of dimethyl sulphide and dimethyl disulphide is regulated in some jurisdictions as part of regulations limiting ambient air concentrations for total reduced sulphur (TRS). British Columbia's Ambient Air Quality Objectives for the Forest Industry require that ambient TRS concentrations, in local communities surrounding a pulp mill, not exceed a maximum of 5 ppb, as an hourly average, or a daily average of 2 ppb (Pollution Control Board, 1989). The ambient air quality in Squamish, the community next to the Western Pulp Limited Partnership bleached kraft pulp mill, consistently meets these TRS limits (personal communication, Taylor J., 1996, Western Pulp Limited Partnership, Squamish, Canada). No surveys have been done on the ambient air concentration for methanol in bleached kraft pulp mills.

Ambient air concentrations of volatile compounds such as hydrogen sulphide and methyl mercaptan are likely to increase if the evaporator condensate, which contains these RSC compounds, are reused. This would increase the concentration of these compounds in the process water increases (Venkatesh et al., 1977; Jain, 1996; Jett, 1995; NCASI, 1994c-g). As discussed, the ambient air concentrations for hydrogen sulphide periodically exceed the ACGIH standards and the ambient air concentrations for methyl mercaptan often exceed these standards. Therefore, an increase in the concentration of hydrogen sulphide or methyl mercaptan in the process water will likely produce conditions under which ambient air concentrations of these RSC consistently exceed the ACGIH standards.

Liquid Phase Regulations

In addition to the ACGIH ambient air quality standards, the United States also has Liquid Phase Regulations as part of the Cluster Rule for kraft pulp mills (Vice and Carroll, 1998). These regulations attempt to control ambient air quality by controlling the amount of HAP and foul odorous compounds present in the process water that could volatilize to the atmosphere. Since methanol is by far the most abundant volatile contaminant contained in kraft pulp and paper mill wastewater, the Cluster Rule uses methanol as a surrogate for all HAP and odorous compounds. Unlike the ACGIH ambient air quality standards, the Cluster Rule regulations are not based on exposure information but are on based on maximum achievable control technology (MACT). That is, they are based on the efficiency of the best performing technologies available to remove the HAP and foul odorous compounds from the condensate and prevent them from volatilizing to the atmosphere. Under the MACT portion of the Cluster Rule, to ensure adequate ambient air quality, the evaporator condensate must be treated at the source to achieve the removal efficiencies listed below, before the evaporator condensate can be sewered and sent to a combined mill effluent biological treatment system for final treatment.

- at least 92 % methanol removal efficiency.
- at least 3.3 kg methanol/tonne of pulp produced (or 5.11 kg methanol/tonnne of pulp produced for bleached mills).
- a maximum methanol concentration of 210 mg/L in the treated final effluent (330 mg/L for bleached mills).

As an alternative to treating the evaporator condensate at the source, the Cluster Rule indicates that the pulping process units could be sealed and the process wastewater hard-piped to the combined mill effluent biological treatment system using a submerged inlet. This would prevent the emission of HAP or foul odorous compounds to the atmosphere within the mill. This option may not be feasible for older mills that cannot ensure that all of the foul odorous compounds or HAP in the evaporator condensate are contained. Also, for some mills, the piping distances may be excessively long, making the hard-

piping option prohibitively expensive. Also, hard-piping of the evaporator condensate to the combined mill effluent biological treatment system may simply delay and displace the emission of HAP and foul odorous compounds to the atmosphere.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI, 1994a) recommends that the concentration of methanol in the treated evaporator condensate be much lower than the values required by the Cluster Rule (i.e 210 or 330 mg/L) these values if the evaporator condensate is to be reused as process water. In specifying the requirements for systems treating evaporator condensate for reuse, NCASI (1994a) recommends that the concentration of methanol in the treated condensate be less than 20 mg/L.

2.2.2 Disruption of Pulping Process and Pulp Quality

Only a few studies have investigated the effects of reusing evaporator condensate on pulp quality. Annola et al. (1995) investigated the reuse of untreated foul evaporator condensate for washing oxygen-delignified pulp prior to hydrogen peroxide and ozone bleaching. They observed a slight increase in the kappa number and a slight decrease in the brightness of the bleached pulp when untreated foul evaporator condensate was used. The difference was attributed to a higher consumption of bleaching chemicals by the organic compounds present in the reused untreated evaporator condensate. Annola et al. (1995) also observed the formation of potentially hazardous by-products, from the organic compounds contained in the foul evaporator condensate when investigating potential process wastewater reuse options. They observed that a significant amount of formaldehyde, which is classified as a HAP, was formed from methanol contained in the process water, during bleaching. Niemela et al. (1999) investigated the reuse of untreated evaporator condensate at several bleaching stages. No deleterious effects on pulp properties (smell, brightness, kappa number and viscosity) were observed when using clean and combined condensates. However, the use of foul condensate negatively impacted some of the pulp properties (reduced brightness and increased odor).

Sebbas (1987) and Riippa et al. (1999) suggested that particulate material in reused evaporator condensate can clog heating surfaces, screens and shower nozzles. Particulate material can also potentially cause deposits on the pulp products. In specifying the requirements for systems treating evaporator condensate for reuse, NCASI (1994a) recommends that the concentration of suspended solids in the treated condensate be less than 20 mg/L.

2.2.3 Biological Growth in Process Piping and Equipment

Reusing evaporator condensate will likely increase the concentration of organic material in process water. This in turn, can lead to the growth of microorganisms and formation of biological slime on piping and equipment surfaces (Mittelman and Geesey, 1987; Casey, 1960). Biological slime can disrupt normal mill operation by plugging process piping, wires and felts and enhance the rate of corrosion of piping and equipment (Jain, 1995; Casey, 1960). In addition, the biological slime can produce dirty and odorous paper products, reduce the strength of the paper products as well as cause breaks in the paper machine (Casey, 1960).

Biological growth can be controlled by adding biocides to the process flow. However, adding biocides increases the chemical complexity of the process water which, in turn, can potentially disrupt the pulping or paper-making processes and increase the toxicity of the process flow that is discharged to the environment. As an alternative, biological slime formation can be controlled by preventing the growth of bacteria by removing or minimizing the presence of organic material in the process water (Mittelman and Geesey, 1987).

2.2.4 Energy Recovery

The temperature of evaporator condensate typically ranges from 55 to 70 °C (Zuncich et al., 1993; Sebbas, 1987). Treating and reusing the evaporator condensate as process

water in this temperature range would allow the heat content of the evaporator condensate to be recovered. This would significantly reduce the energy requirements associated with heating of make-up water to the required process operating temperature. In addition, the cost associated with cooling the evaporator condensate before treatment, as required for conventional biological treatment, would also be avoided (NCASI, 1994a). The operating temperatures for the various pulping processes in which treated evaporator condensate could be used are listed in Table 2.4.

Table 2.4

Operating Temperature of Pulping Processes

Process	Temperature	Comment
Kraft Cook Liquor	70 °C	Temperature at which cook liquor is introduced
Brown Stock Washing	90 - 150 °C	Depending on the wash procedure. Higher temperature minimizes energy requirements of black liquor evaporation
Bleaching Cl_2 Cl_2/ClO_2	 3 - 20 °C 70 °C	Cl_2 bleaching rate does not increase with temperature and typically proceeds at raw feed-water temperature. Cl_2/ClO_2 bleaching rate increases with temperature
Wet End Additives	90 - 120 °C	Function of the type of chemical additives
Paper Machine	65 °C	Higher temperature increases dewatering and drying efficiency
Causticizing	90 - 100 °C	High temperature is needed for reaction to proceed efficiently
White Liquor Clarifier	100 °C	Typically faster settling rates at higher temperature

(Adapted from Smook, 1992)

Wilson and Hrutfiord (1996) suggested that reusing process wastewater as process water could potentially result in a thermal build-up within the mill. This could increase the rate of corrosion in the mill and also decrease the bleaching efficiency in conventional bleach plants (Smook, 1992). However, the excess heat can also be considered as a commodity and used for heating the buildings at the pulp mill as well as the houses in the surrounding community (as is the case at the E.B. Eddy pulp mill in Espanola, Ontario, Canada).

2.2.5 Summary of Treatment Requirements for Reuse

As presented in Sections 2.2.1 to 2.2.4, the treatment requirements for the reuse of evaporator condensate are the following.

1. NCASI (1994a) suggests that for reuse, the concentration of methanol in the treated condensate should be less than 20 mg/L.
2. Hydrogen sulphide and methyl mercaptan should be completely removed from the evaporator condensate before reuse as process water to prevent any further increase in their ambient air concentrations at kraft pulp mills.
3. The organic content of the evaporator condensate should be reduced as much as possible before reuse to minimize the consumption of bleaching and other process chemicals, to minimize the formation of potentially hazardous by-products and to prevent any negative impacts on the pulping process and pulp products.
4. The treated evaporator condensate should contain no suspended solids that could potentially clog process showers when reused.
5. The evaporator condensate should not be cooled prior to treatment to maximize the energy recovery during reuse and to reduce costs that otherwise would be associated with cooling as required for conventional biological treatment.

2.3 Evaluation and Selection of Treatment Technology

Three technologies have previously been investigated by others for the treatment of evaporator condensate. These are:

1. steam stripping,
2. anaerobic biological treatment, and
3. aerobic biological treatment.

2.3.1 Steam Stripping

A number of kraft pulp mills currently steam strip foul evaporator condensate before sewering and treatment in a combined mill effluent secondary biological treatment system and subsequent discharge to the environment. The stripped volatile compounds are typically burned in the lime kiln, the recovery boiler or in a designated incinerator (McCance and Burke, 1980). The performance of steam strippers in removing the contaminants of concern from evaporator condensate has been investigated in a number of industry surveys (McCane and Burke, 1980, NCASI, 1994b).

McCance and Burke (1980) reported that mills using steam strippers with a steam to evaporator condensate ratio of more than 8 % by weight could typically achieve more than 95 % RSC removal and a maximum of approximately 75 % methanol removal. A steam to evaporator condensate ratio of approximately 18 to 20 % by weight was required to consistently achieve 90 % methanol removal (Vora and Venkataraman, 1995; NCASI, 1994b; Zuncich et al., 1993). For methanol removal efficiencies of greater than 90 %, the amount of steam required for stripping increases significantly (Zuncich et al., 1993). The costs associated with providing such a large amount of steam can make steam stripping prohibitively expensive (Vora and Venkataraman, 1995). As an alternative, waste heat from the blow heat recovery system could be used to meet the steam requirements for a stripper system (Hough and Sallee, 1977; Farr et al., 1993). This

could reduce the operating cost for steam by as much as one order of magnitude. However, significant modifications to existing mill equipment would be required (Farr et al., 1993; NCASI, 1994b). Consequently, waste heat recovery for steam stripping may only be feasible with newer mills. The total organic carbon removal efficiency achieved by steam stripping is typically lower than that of methanol. Danielsson and Hakansson (1996) reported that the total organic carbon removal (measured as COD) efficiency was approximately 48 to 97 % of the removal efficiency for methanol, depending on the characteristics of the evaporator condensate. The lower COD removal efficiency was attributed to the presence of non- and semi-volatile compounds in evaporator condensate.

Although relatively efficient for the removal of volatile contaminants from evaporator condensate, steam strippers are not capable of removing non- or semi-volatile contaminants or particulate material.

2.3.2 Anaerobic Biological Treatment

Anaerobic biological treatment has been considered as an alternative to steam stripping for the treatment of evaporator condensate mainly because of the potential savings associated with the low operating costs of the process. Relatively high COD and methanol removal efficiencies have been reported for anaerobic biological treatment systems treating kraft pulp mill evaporator condensate. Qiu et al. (1988) reported a COD removal efficiency of approximately 70 % using an up-flow sludge blanket system at a loading rate of 12 kg COD/m^3·day. Wiseman et al. (1998) reported soluble COD and methanol removal efficiencies of 86 and 99 %, respectively, using an up-flow sludge blanket system at loading rates ranging from 20 to 25 kg COD/ m^3·day. Norman (1983) reported an 80 % COD removal efficiency using an anaerobic fluidized bed system at a loading rate of 13 kg COD/ m^3·day. Yamaguchi et al. (1990) reported a 90 % BOD removal efficiency using a fixed film system at a loading rate up to 34.5 kg BOD/m^3·day. Welander et al. (1999) estimated a COD removal efficiency of approximately 90 % using an attached growth system at a loading rate of 20 to 25 kg COD/m^3·day. However,

Welander at al. (1999) also observed a significant reduction in COD removal efficiency, down to approximately 20 %, when the operating temperature was increased to above 50 °C, even when the loading rate was reduced to less than 10 kg COD/m^3·day. A similarly low BOD removal efficiency was not observed by Yamaguchi et al (1990) when treating evaporator condensate in a fixed bed system at an operating temperature of 53 °C with loading rates of up to 34.5 kg BOD/m^3·day.

Relatively low removal efficiencies have also been reported in some studies. Barton et al. (1998) reported a 67.4 % COD removal efficiency (81.5 % methanol removal) for an up-flow sludge blanket system at loading rates ranging from 10 to 20 kg COD/m^3·day. When treating combined mill condenstes, Carpenter and Berger (1984) reported a 40 % BOD removal efficiency for an up-flow sludge blanket system and a submerged media system at a loading rate of 16 kg BOD/m^3·day. Welander et al. (1999) reported a 60 % COD removal efficiency in a full scale suspended carrier system treating a mixture of pulp mill condensates. It was suggested that the lower treatment efficiency observed in these systems could be attributed to the contaminants present in the condensate matrix. Pipyn et al. (1987) and Yamaguchi et al. (1990) suggested that pre-stripping, to remove RSC from the condensate, is required to ensure stable operation in an anaerobic biological system.

Although the reported COD removal efficiencies are in general relatively high, the residual COD concentration in the treated effluents are also relatively high. Yamaguchi et al. (1990) reported that the treated effluent from a fixed bed system had a COD concentration of approximately 800 mg/L. Cocci et al. (1985) reported effluent COD concentrations ranging from 500 to 2500 mg/L for a geo-textile media down-flow anaerobic filter system. Wiseman et al. (1988) reported effluent COD and BOD of 695 and 185 mg/L, respectively, using an upflow sludge blanket. Barton et al. (1998) reported effluent COD and methanol concentrations of 1859 and 641 mg/L, respectively for an up-flow sludge blanket system. Pipyn et al. (1987) reported an effluent COD concentration of 1500 mg/L using an attached growth system. Norman (1983) reported an effluent COD concentration of approximately 280 mg/L using a fixed bed reactor.

Some of the reported residual effluent COD and BOD may be due in part to suspended solids in the treated effluent. Qiu et al. (1988) reported that the suspended solids concentration in the treated effluent increased with the loading rate for an upflow sludge blanket system. At a loading rate of 3 kg COD/m^3·day, the effluent suspended solids concentration was approximately 80 mg/L and at a loading rate of 15 kg COD/m^3·day, the effluent suspended solids concentration was approximately 130 mg/L. However, Pipyn et al. (1987) found no relationship between loading rate and effluent suspended solids concentration using an anaerobic attached growth system. The observed effluent suspended solids concentrations ranged from 7 to 33 mg/L. Cocci et al. (1985) reported an effluent suspended solids concentration that ranged from approximately 20 mg/L to more than 400 mg/L using a geo-textile media down-flow system. Barton et al. (1998) reported an effluent solids concentration of approximately 184 mg/L for an up-flow sludge blanket system. Yamaguchi et al. (1990) reported an effluent suspended solids concentration 300 to 400 mg/L for a fixed bed system. When the fixed bed was coupled to a membrane, the effluent from the system contained virtually no suspended solids.

There is limited information regarding the removal of RSC from evaporator condensate using anaerobic biological treatment. Qiu et al. (1988) observed a 38 and 30 % reduction in the concentration of the inorganic and organic sulphur compounds, respectively, during treatment using an up-flow sludge blanket system. These sulphur compounds were reduced to sulphide and then were subsequently removed with the off-gas during treatment. Barton et al. (1998) observed a 38, 5 and 84 % reduction in the concentration of hydrogen sulphide, dimethyl sulphide and dimethyl disulphide, respectively, for an upflow sludge blanket. There was a 70 % increase in the concentration of methyl mercaptan. This was likely due to the reduction of dimethyl disulphide to methyl mercaptan. The RSC removed during treatment were accounted for in the off-gas. Cocci et al. (1985) also investigated the removal of sulphur compounds during treatment using a geo-textile media down-flow filter. The total sulphur concentration was reduced by approximately 25 % on average. However, it is not clear if the sulphur compounds were reduced to hydrogen sulphide and subsequently removed with the off-gas or simply volatilized with the off gas.

2.3.3 Aerobic Biological Treatment

Aerobic biological treatment has also been considered as an alternative to steam stripping for the treatment of evaporator condensate. The main advantages of aerobic biological treatment over anaerobic biological treatment are the ability to achieve higher contaminant removal efficiencies and the ability to oxidize RSC. In addition, aerobic systems are typically more resistant to toxic substances than anaerobic treatment systems (Sierra-Alrarez et al., 1994).

Welander et al. (1999) and Qiu et al. (1988) investigated the treatment of anaerobically treated evaporator condensate using aerobic treatment. They observed an additional 20 to 30 % reduction in the concentration of COD compared to anaerobic treatment alone. Barton et al. (1998) reported much higher methanol and COD removal efficiencies when treating foul evaporator condensate using a completely mixed activated sludge system, compared to an anaerobic up-flow sludge blanket system. The loadings to the aerobic and anaerobic systems were 0.88 g BOD/g MLVSS·day and 10 to 20 kg COD/m^3·day, respectively. The methanol and COD removal efficiencies were more than 99 and 92 %, respectively, for the activated sludge system and 81 and 67.4 %, respectively, for the anaerobic up-flow sludge blanket. The residual methanol and COD concentrations were less than 97 and 416 mg/L, respectively, for the activated sludge system and 645 and 1859 mg/L, respectively, using the anaerobic up-flow sludge blanket. In another study, Barton et al. (1996) reported a residual methanol and BOD concentration of less than 0.3 mg/L and 25 mg/L, respectively, when treating evaporator condensate using a batch activated sludge system. Milet and duff reported over 99 % methanol and approximately 64 to 88 % COD removal when treating evaporator condensate using a feed-back controlled sequencing batch reactor. Cook et al. (1973) observed an 80 and 98 % removal efficiency for COD and methanol, respectively, when treating combined mill condensate using an activated sludge system. When using the same system, but without biomass, the observed COD and methanol removal efficiencies were only 8.3 and –5.7 %, respectively. Although this indicates that although some volatile contaminants can be stripped to the atmosphere during aerobic biological treatment, the higher COD removal

efficiencies observed for aerobic systems did not appear to be due to the stripping of contaminants due to the aeration system. Milet and Duff (1999) suggested that the removal of RSC was due mostly to stripping.

Barton et al. (1998) observed much higher RSC removal efficiencies during aerobic treatment than during anaerobic treatment. On average, more than 95 % of the RSC were oxidized during aerobic treatment. Qiu et al. (1988) reported that aerobic post-treatment oxidized all of the hydrogen sulphide contained in the effluent from the anaerobic system to non-odorous and non-hazardous sulphate. Mahmood et al. (1999) suggested that the higher observed RSC removal in aerobic treatment systems is due mostly to the rapid abiotic oxidation of the sulphur compounds. They observed that, in the presence of oxygen and the micro-nutrients necessary for biological treatment, hydrogen sulphide is rapidly abiotically oxidized. Chen and Morris (1972) and Wilmot et al. (1988) also reported that aqueous RSC are rapidly oxidized in the presence of oxygen, at the pH range necessary for biological treatment.

Aerobic treatment also appears to be more effective at removing trace HAP contained in evaporator condensate. Barton et al. (1998) observed that during aerobic treatment of evaporator condensate, the concentrations of methyl ethyl ketone and acetaldehyde were reduced to below detection limits, while only approximately 50 % was removed during anaerobic treatment. Cook et al. (1973) also observed a high MEK removal efficiency in an activated sludge system treating combined mill condensate. Wilson and Hrutfiord (1975) reported that the concentration of terpentine contained in kraft pulp mill effluents could be reduced by 65 to 90 % during aerobic treatment. However, based on the results reported by Cook et al. (1973), it is not clear if the removal of terpentine from the condensate was due to biological uptake or stripping to the atmosphere due to the aeration system.

Aerobic treatment systems are typically more resistant than anaerobic systems to toxic substances or shock loads (Sierra-Alrarez et al., 1994). Also, the color associated with the treated effluent from an aerobic biological treatment system is less objectionable than

the color associated with the treated effluent from an anaerobic treatment system. Barton et al. (1998) reported that the effluent from an activated sludge system treating evaporator condensate was generally free of color or had a light gray color, while the effluent from an anaerobic USAB treating evaporator condensate had a dark gray color.

However, like anaerobic biological treatment systems, conventional aerobic biological treatment systems also tend to have relatively high concentrations of suspended solids in their effluent. Barton et al. (1998) reported an effluent concentration of approximately 132 mg/L using an activated sludge system. In another study, Barton et al. (1996) reported a supernatant suspended solids concentration of approximately 70 mg/L in a batch activated sludge system. Milet and Duff (1999) reported effluent suspended solids concentrations ranging from 230-270 mg/L from a sequencing batch reactor (no effort was made to control the effluent solids concentration). In addition, the operating temperature for conventional aerobic biological treatment systems is typically limited to less than 35 °C. One of the main problems associated with treating wastewaters at a higher temperature is the deterioration of the sludge settling characteristics. Tripathi and Allen (1998) reported a decrease in sludge settling characteristics at higher operating temperatures when treating bleached kraft pulp mill effluent using a sequencing batch reactor. The formation of dispersed, pinpoint flocs at higher operating temperatures (60 °C versus 35 °C) was responsible for the poorer settling characteristics. The effluent suspended solids concentrations at operating temperatures of 35 and 60 °C were 15 mg/L and 70 mg/L, respectively. Flippin and Eckenfelder (1994) also reported higher effluent suspended solids concentrations and poorer sludge settling characteristics at higher operating temperatures.

2.3.4 High Temperature Aerobic Biological Treatment

The temperature of the evaporator condensate stream typically ranges from 55 to 70 °C (Zuncich et al., 1993; Sebbas, 1987). Aerobic biological treatment for reuse of evaporator condensate as process water in this temperature range would permit the heat

content of the evaporator condensate to be recovered. This could result in energy savings as discussed in Section 2.2.4.

A literature review by LaPara and Alleman (1999) indicated that at higher temperatures, contaminant removal efficiencies and removal rates are typically higher for aerobic biological treatment systems. Therefore, high temperature operation may not only result in cost savings due to energy recovery, but could also result in higher treatment efficiencies than reported for conventional biological systems treating evaporator condensate.

A literature search preceding the present study did not reveal any published information regarding the treatment of evaporator condensate using a high temperature aerobic biological treatment system. However, a limited number of studies have investigated the consumption of methanol by mixed microbial cultures at elevated temperatures. Snedecor and Cooney (1974) investigated the growth of a mixed bacterial culture with methanol as a sole substrate at temperatures ranging from 45 to 65 °C. The study indicated that the mixed culture exhibited a maximal observed growth yield at an operating temperature of 58 °C. Izumi et al. (1989) reported similar results when investigating the activity and stability of formate dehydrogenase, an enzyme involved in the oxidation of methanol, at temperatures ranging from 20 to 70 °C. The maximum specific activity was reported at a temperature of approximately 55 °C and the enzyme was stable up to a temperature of approximately 60 °C. The consumption of RSC at elevated temperatures by pure cultures has also been investigated. Kargi and Robinson (1982, 1984) and Kargi (1987) reported that a pure culture of thermophilic sulphur oxidizing bacteria (*Sulpholobus acidocaldarius*) could biologically oxidize a number of RSC such as thiosulphides, sulphides, thiophene dibenzothiophene, thianthrene and thioxanthene to CO_2 and SO_4^{2-}. Other types of thermophilic sulphur oxidizing bacteria have also been reported to oxidize sulphur compounds at temperatures ranging from 55 to more than 100 °C (Brock, 1978; Brock et al., 1994).

High temperature aerobic biological treatment appears to be a promising technology for the removal of contaminants of concern from evaporator condensate. However, a number of potential disadvantages are associated with conventional aerobic biological treatment systems operating at a high temperature. First, the effluent suspended solids concentration from a conventional aerobic biological treatment system is relatively high and would be expected to be even higher at higher operating temperatures as previously discussed. This can result in a relatively high concentration of suspended solids in the treated effluent. Second, conventional aerobic biological treatment systems have an open configuration where the process mixed liquor is generally open to the atmosphere at a number of locations throughout the treatment process. This can cause a number of problems associated with the stripping of HAP and foul odorous compounds from the treatment system due to the aeration system. In addition, in an open system, the microorganisms can be exposed to significant temperature gradients and fluctuations. This can significantly impact their activity, resulting in a decrease in the treatment efficiency (Brock, 1978). Third, the footprint associated with a conventional aerobic biological treatment system can be relatively large. This is of concern in many pulp and paper mills where limited area is available to install a system for treating evaporator condensate for reuse.

High Temperature Aerobic Membrane Bioreactor

As an alternative to a conventional aerobic biological treatment system, an aerobic membrane bioreactor (MBR) was considered for the high temperature aerobic biological treatment of evaporator condensate for reuse. An MBR is similar to a conventional activated sludge system with the exception that the clarifier is replaced with an ultrafiltration membrane.

An MBR has a number of advantages over conventional aerobic biological treatment systems. First, the membrane component of the MBR retains all of the mixed liquor suspended solids (MLSS). Therefore, the suspended solids concentration in the treated effluent is not limited by the settling characteristics of the MLSS. The resulting treated

effluent contains virtually no suspended solids. Zaloum et al. (1996) reported an effluent suspended solids concentration of 0 mg/L from an MBR. The MLSS concentration in the MBR was 2300 mg/L. Dufresne et al. (1998) reported over 99% removal of suspended solids during treatment of chemithermomechanical pulp mill effluent. The MLSS concentration in the MBR ranged from 7700 to over 31000 mg/L. Riippa et al. (1999) reported complete removal of suspended solids during treatment of thermomechanical pulp mill effluent using an MBR. Second, since all of the MLSS can be retained, very high biomass concentrations can be maintained in the MBR. Biomass concentrations ranging from 10000 up to 30000 mg/L (as MLSS) can be achieved in an MBR (Krauth and Staab, 1993; Dufresne et al., 1998; Sato and Ishii, 1991; Magara and Itoh, 1991). This allows high loading rates to be imposed on the MBR, resulting in a relatively small system size. However, the pseudo steady state permeate flux through the membrane component of the MBR tends to decrease at higher operating MLSS concentrations as presented below and further discussed in Section 8.3. Third, since the removal of biosolids from an MBR is only due to sludge wastage, the hydraulic retention time and the sludge retention time can be controlled independently, allowing better control over the treatment system performance (Dufresne et al., 1998; Trouve et al., 1994). Fourth, an MBR can be designed as a closed system (Krauth and Staab, 1993). Consequently, the emission of HAP and FOC to the atmosphere can be minimized. In addition, since the system is closed, the microorganisms are not exposed to large temperature gradients.

However, an MBR has one main disadvantage. The permeate flux through the membrane component of an MBR tends to decrease over time. The decline in the permeate flux is mostly due to the formation and evolution of a secondary layer, which consists mainly of microorganisms and their associated extracellular matrices as well as particulate material adsorbed from the waste stream, on the membrane surface (Shimizu et al., 1993; Riesmeier and Kroner, 1987; Datar, 1984; Reed et al., 1993; Lojkine et al., 1992; Sato and Ishii, 1991; Yamamoto et al., 1989).

The rate and extent of the decline has been reported to increase at higher MLSS concentrations believed to be due to a higher rate of solids migration from the bulk solution to the membrane surface. Sato and Ishii (1991) and Magara and Itoh (1991) proposed that the pseudo steady state permeate flux can be related to the MLSS concentration as presented in Equation 2.1:

$$J_{SS} \propto (MLSS)^{-n} \qquad (2.1)$$

where Jss is the pseudo steady state permeate flux ($L/m^2 \cdot hour$), α is the proportionality symbol, MLSS is the mixed liquor suspended solids concentration and n is a power constant (-).

Their results suggest that the reduction in the pseudo steady state permeate flux at a high MLSS concentration can be offset by increasing the cross-flow velocity over the membrane to increase the rate of back diffusion of the solid particles (Cheryan, 1986). Shimizu et al. (1993) and Magara and Itoh (1991) reported that the pseudo steady state permeate flux increased linearly with the cross-flow velocity. Also, the pseudo steady state permeate flux through a membrane increases at higher temperatures (Cheryan, 1986). Therefore, for a high temperature MBR, the pseudo steady state permeate flux should be higher than for an MBR operating at a lower temperature.

The reduction in the permeate flux at higher MLVSS concentrations has also been attributed to an increase in the bulk viscosity at higher biomass concentrations (Ben Aim, 1999; Nagaoka et al., 1996). The increase in the bulk viscosity at higher MLVSS concentrations can reduce the shear over a membrane surface (i.e lower the Reynolds number) which in turn decreases the back diffusion coefficient. Lubbecke et al. (1995) observed no effect of the MLVSS concentration on the permeate flux when turbulent conditions were maintained over a membrane surface. However, they observed that the flux declined at higher MLVSS concentrations, as reported by Sato and Ishii (1991) and Magara and Itoh (1991), when laminar conditions were maintained over the membrane

surface. Therefore, it appears that the MLVSS concentration may have no effect on the permeate flux if turbulent conditions are maintained over a membrane surface.

2.3.5 Evaluation of Technologies for the Treatment of Evaporator Condensate for Reuse

Based on the treatment requirements summarized in Section 2.2.5 and the literature review presented in Sections 2.3.1 to 2.3.4, the following summary table was developed (Table 2.5). A high temperature aerobic MBR appeared to be the most promising technology for the treatment of evaporator condensate for reuse. High temperature aerobic biological treatment using an MBR can potentially achieve higher methanol, RSC and trace organic compound removal efficiencies than anaerobic biological treatment or steam stripping. The membrane component of the MBR would ensure that the treated effluent contains virtually no suspended solids. Because of its closed configuration, an MBR could be operated at a high temperature without exposing the microorganisms in the treatment system to significant temperature fluctuations and emissions of HAP and odorous compounds can be minimized. Finally, because of the high temperature operation, the heat content of the evaporator condensate can be recovered.

In addition to the above advantages, an MBR is also typically much smaller than other conventional biological treatment systems. This is of importance in many mills where little space is available to install new processes.

From hereon, aerobic biological treatment will be referred to as biological treatment. Similarly, an aerobic MBR will be referred to as an MBR.

2.4 Summary

Methanol and reduced sulphur compounds (RSC) were identified as the primary contaminants of concern contained in evaporator condensate. These contaminants are of

concern primarily because they are hazardous air pollutants (HAP) and/or foul odorous compounds. Reusing evaporator condensate in a kraft pulp mill without treatment can result in subsequent emission of HAP and foul odorous compounds and generate unpleasant or even hazardous working conditions for mill staff. Some trace organic contaminants contained in evaporator condensate are also of concern primarily because they could disrupt the pulping process or impact pulp quality. A number of conventional technologies were considered for the treatment of evaporator condensate for reuse. However, the relatively poor treatment efficiencies and/or high costs associated with these conventional systems provided incentives to investigate and develop a better treatment technology. A high temperature membrane bioreactor was selected as the most promising novel technology for the treatment of evaporator condensate for reuse.

Table 2.5

Summary of the Evaluation of Potential Technologies for the Treatment of Evaporator Condensate

Treatment Requirements	***Steam Stripping**	***Anaerobic Treatment**	***Aerobic Treatment**	**High Temperature MBR**
Ability to remove methanol	Moderate	Moderate	Good	Potentially good
Ability to remove RSC	Good	Moderate	Good	Potentially good
Ability to remove non-methanolic contaminants	Moderate to poor	Moderate	Good	Potentially good
Suspended Solids in Effluent	Relatively low	Relatively high	Relatively high	None
Cooling Required	None	Possibly	Yes	None

(* conventional treatment technologies)

Chapter 3 – Bench Scale High Temperature Membrane Bioreactor

3.1 Configuration

A schematic of the MBR used for the different experiments is presented in Figure 3.1. The MBR consisted of an aerated reactor tank, a ceramic tubular ultrafiltrafiltration membrane (Membralox 1T1-70 bench scale filtration unit: 7 mm ID, 0.0055 m^2 surface area, 500 angstrom pore size), a progressive cavity pump (Moyno Model SP 33304) and a pre-heating tank.

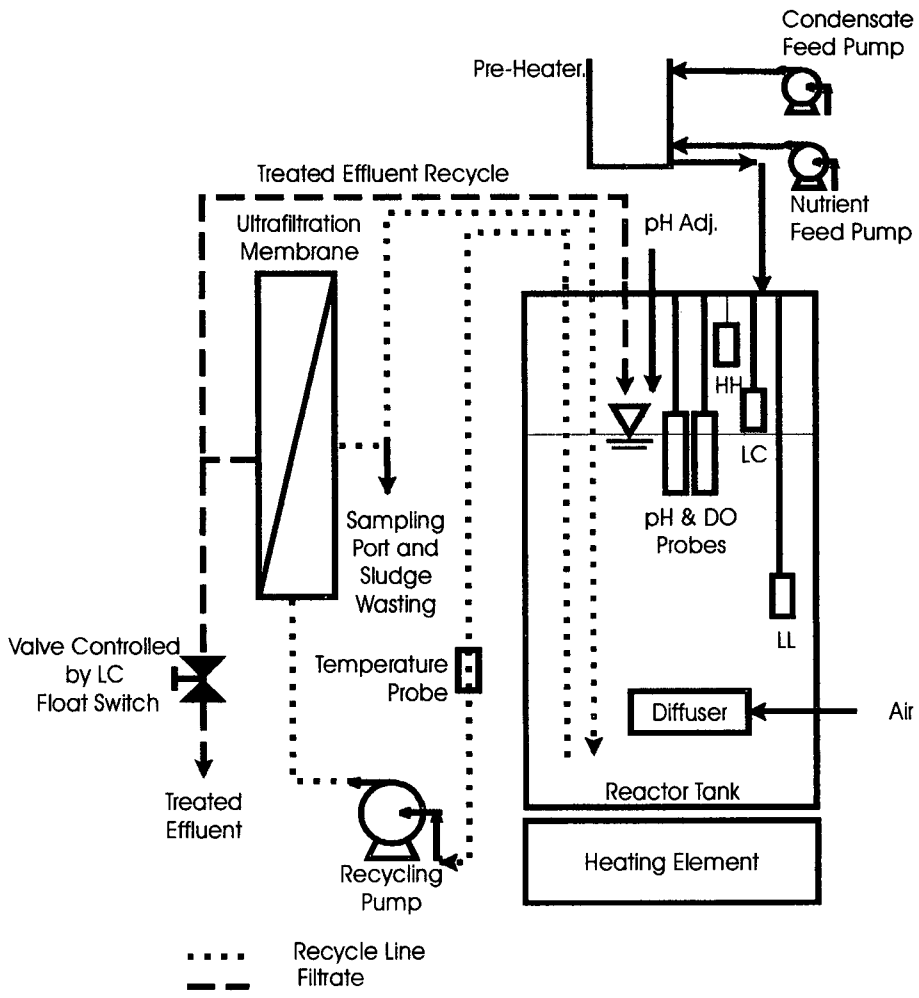
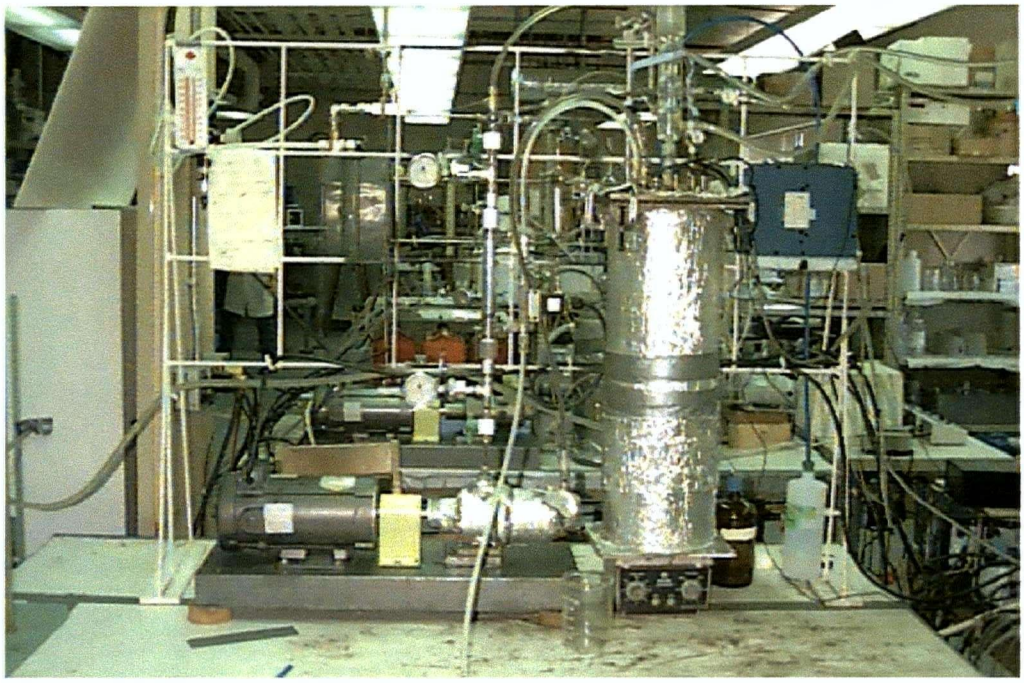


Figure 3.1 - Schematic of Bench Scale High Temperature MBR
(LC: level control float switch; HH: high level emergency shut-off float switch; LL: low level emergency shutoff float switch)

Three bench scale high temperature MBRs were used during the different experiments. When investigating contaminant removal from synthetic condensate, two MBRs, a primary and a secondary, both with an 8 litre working volume, were used. The reactor tank component of the primary MBR was constructed of stainless steel and the reactor tank component of the secondary MBR was constructed of Plexiglas. The primary bench scale MBR is shown in Picture 3.1. When investigating contaminant removal from real condensate, an MBR with a 1.79 litre working volume was used. The smaller reactor volume was used to minimize the amount of real evaporator condensate that needed to be shipped from the Western Pulp Limited Partnership bleached kraft pulp mill (Squamish, Canada) to the laboratory facilities where the bench scale MBR was located. The type of reactor used is indicated in the experimental procedures and equipment set-up section at the start of each experiment, presented in Chapters 4 to 7 and summarized in Table 3.1. All MBR components were insulated to minimize temperature fluctuations.



Picture 3.1 - Picture of Primary Bench Scale High Temperature MBR

A ceramic ultrafiltration membrane was selected for the bench scale MBR. A ceramic membrane was selected over a polymeric membrane because of its proven track record for operating under extreme conditions such as high temperatures.

Excessive foaming was initially observed in the headspace of the reactor tank component of the MBR when using real evaporator condensate as feed. To prevent foaming, a shower head was installed in the headspace of the small MBR on the return line.

3.2 Operation

The MBR was fed semi-continuously by adding a mixture of evaporator condensate and nutrients, once every 3 hours. Semi-continuous feeding was chosen because it can yield more information about removal kinetics than experiments performed under strict continuous flow conditions. The feed was pre-heated to prevent excessive temperature fluctuations in the MBR. The feed was pumped (Masterflex pump) to a 1 litre stainless steel tank where it was preheated with a stainless steel heating coil until the temperature of the feed was approximately equal to that of the operating temperature of the MBR. A solenoid valve, located at the bottom of the pre-heating tank, opened automatically when the temperature of the feed in the pre-heating tank reached the desired set point allowing the feed to be added to the MBR. Synthetic, real and mixtures of both synthetic and real evaporator condensates were used as feed. The exact composition of the feed is indicated in the experimental procedures and equipment set-up section at the start of each experiment, presented in Chapters 4 to 7 and summarized in Table 3.1. The characteristics of the synthetic and real evaporator condensate and the procedure used to store them are presented in Appendix 2. The composition of the nutrient solution remained constant throughout the study. The characteristics of the nutrient solution were selected to ensure non-nutrient limiting conditions. The characteristics of the nutrient solution used are presented in Appendix 3.

The initial hydraulic retention time (HRT) was selected to achieve over 95 % methanol removal efficiency. A specific methanol utilization coefficient of 0.45/day and a mixed liquor volatile suspended solids (MLVSS) concentration of 2500 mg/L, as observed by Barton et al. (1996), for a batch activated sludge system treating evaporator condensate at an operating temperature of 33 °C, were used to estimate the initial required HRT. Based

on an influent methanol concentration of 500 mg/L, as was initially measured in the evaporator condensate from the Western Pulp Limited Partnership kraft pulp mill, a minimum HRT of slightly over 10 hours was calculated to be required. An HRT of 12 hours was initially selected for this study. The HRT was controlled by maintaining a constant mixed liquor volume in the reactor tank. This was done by discarding the treated effluent (permeate) at the start of each batch feed cycle following the addition of the evaporator condensate, when the liquid volume in the reactor tank was too high, and by recycling the treated effluent back to the reactor tank when the required liquid level had been reached. A level control switch controlled the recycling of the treated effluent as illustrated in Figure 3.1. A volume of treated effluent equivalent to the volume of evaporator condensate added to the reactor tank as feed was discarded during each batch feed cycle.

A relatively long sludge retention time (SRT) was selected to maintain a biomass inventory (MLVSS) of approximately 2500 mg/L in the MBR. Based on an observed yield of approximately 0.3 as reported by Snedecore and Cooney (1974) for the growth of a mixed microbial culture on methanol as a sole substrate at elevated temperatures, a minimum SRT of approximately 17 days was calculated to be required. A relatively long SRT was also selected to provide sufficient residence time for any poorly degradable organic compounds contained in evaporator condensate to adsorb to biomass and subsequently be biologically oxidized. A 20 day SRT was selected for this study. The SRT was controlled automatically by wasting a preset volume of mixed liquor from the recycling line at the start of every batch feed cycle using a Masterflex pump as illustrated in Figure 3.1.

The pH of the mixed liquor in the MBR was controlled using a pH meter/controller that added sodium hydroxide or hydrochloric acid as required. The pH was maintained above 6 (approximately 6.5) except during the first experiment as presented in Section 4.2 as summarized in Table 3.1. Air was provided through a fine bubble stone diffuser to produce non-limiting dissolved oxygen conditions as presented in Appendix 1. The aeration rates used are indicated in the experimental procedures and equipment set-up

section at the start of each experiment, presented in Chapters 4 to 7. The temperature of the mixed liquor was maintained at a specified set point, ± 2 °C, using a temperature sensor/controller and a heater. The primary and small MBR were heated using hot plates. The secondary MBR was heated using a water jacket through which heated water was circulated. The temperature set points are indicated in the experimental procedures and equipment set-up section at the start of each experiment, presented in Chapters 4 to 7 and summarized in Table 3.1.

The MBR was inoculated with waste sludge obtained from various locations. The waste sludges used to inoculate the MBR for the different experiments are indicated in the experimental procedures and equipment set-up section at the start of each experiment, presented in Chapters 4 to 7 and summarized in Table 3.1.

The ultrafiltration membrane component of the MBR was operated with a cross-flow velocity over the membrane surface of approximately 3 m/s as recommended by the ultrafiltration membrane supplier. This high cross-flow velocity over the membrane surface was required to maintain a relatively high permeate flux through the membrane as discussed in Section 2.3.4. A cross-flow velocity of 3 m/s corresponds to a recycling flow of 2.3 L/minute through the recycling line from the reactor, through the tubular membrane and back to the reactor. The trans-membrane pressure maintained across the membrane surface was approximately 2 atmospheres (30 psi), as recommended by the ultrafiltration membrane supplier. The trans-membrane pressure was maintained using a flow restriction valve on the dowsteam end of the recycling line. Under these operating conditions, the pseudo steady-state permeate flux through the membrane was approximately 162 L/hour•m^2. Therefore, only approximately 0.65 % of the recycling flow permeated through the membrane. The permeate flux through the membrane was monitored throughout the present study as presented in Appendix 9.

3.3 Monitoring

The rate of contaminant removal was determined by measuring changes in the concentration of the contaminant in the MBR over time. Samples were collected and analyzed for the contaminant of concern at regular intervals following the start of selected batch feed cycles. The sample collection frequencies and the analysis performed on the collected samples are indicated in the experimental procedures and equipment set-up section at the start of each experiment, presented in Chapters 4 to 7 and summarized in Table 3.1.

For the first experiment (Chapter 4) and part I of the second experiment (Chapter 5), samples collected for analysis were withdrawn from the sampling port located on the return line downstream of the membrane unit as illustrated in Figure 3.1. For Part II of the second experiment and experiments 3 and 4 (Chapters 6 and 7), samples were collected from the ultrafiltration cartridge effluent line. The membrane casing was drained before sampling to minimize the dilution effect that can occur in the membrane casing. The samples collected from the ultrafiltration cartridge effluent line did not require filtration before analysis and therefore, larger sample volumes could be collected.

Tests using inactivated biomass were used to investigate the abiotic removal of contaminants in the MBR. The biomass was inactivated by adding sodium azide to obtain a 1 % concentration in the mixed liquor (see Appendix 1).

A number of off-line tests were developed to assist in investigating the fate and removal kinetics of the contaminants of concern during treatment using an MBR as presented in the experimental procedures and equipment set-up section at the start of each experiment presented in Chapters 4 to 7. These off-line tests are described in Appendix 1.

The analytical methods used for the analysis of the samples are also presented in Appendix 1.

Table 3.1

Summary of Parameters for the Different Experiments Done Using the Bench Scale High Temperature MBR

Experiment	1-a	1-b	2-a	2-b	3-a	3-b	3-c and 4
Results presented in Chapter(s)	4	4	5	5	6	6	6 and 7
Reactor Used	Primary	Secondary	Primary	Primary	Primary	Small	Small
Condensate Used							
Synthetic	Yes	Yes	Yes	Yes	Yes	Yes	
Real						Yes	Yes
HRT (hours)	12	12	12	12	12	18	18
Operating Temperature	55	55	55-70	60-65	60	60	60
Acclimatization Temperature	55	55	55	60	60	60	60
PH	Neutral	3 to 7	Neutral	Neutral	Neutral	Neutral	Neutral
Parameters Monitored							
Methanol	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Hydrogen sulphide							Yes
Methyl mercaptan							Yes
Dimethyl sulphide	Yes	Yes					Yes
Dimethyl disulphide	Yes	Yes					Yes
MLVSS	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Flux	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Methanol metabolism				Yes	Yes	Yes	Yes
TOC							Yes
Residual TOC				Yes			Yes
Qualitative exam			Yes	Yes	Yes	Yes	Yes
Duration of Test (weeks)							
Acclimatization	6	3	Cont. 1-b	6	3	Cont. 3-a	Cont. 3-b
Steady state	14	18	16	12	4	7	6
Inoculum							
Lab-scale ASS treating BKME	Yes						
Full-scale ASS treating BKME	Yes	Yes		Yes	Yes	From 3-a	From 3-b
Pilot-scale municipal ASS	Yes						
Solids from a hot Spring	Yes						
Bench-scale high Temperature MBR		From 1-a	From 1-a				

(Cont.: continued from previous experiment; From: inoculated with sludge from previous experiment; Temperature in degrees Celsius; Methanol metabolism: monitored off-line using radio-labeled methanol; BKME: bleach kraft pulp mill effluent; AAS: activated sludge treatment system)

Chapter 4 – Feasibility of Simultaneous Biological Removal of Methanol and Reduced Sulphur Compounds from Synthetic Evaporator Condensate at an Elevated Temperature

4.1 Introduction

As presented in Section 2.1, methanol and RSC are the most abundant contaminants present in evaporator condensate. These contaminants must be removed before the evaporator condensate can be reused (Section 2.2). The ability of microorganisms to biologically oxidize methanol and RSC in the expected temperature range for condensate has been investigated by others. Snedecor and Cooney (1974) investigated the effect of elevated temperatures ranging from 45 to 65 °C on the observed growth yield for a mixed culture of methanol-consuming microorganisms. A maximum growth yield was observed at a temperature of approximately 58 °C. Izumi et al. (1989) investigated the effects of temperatures ranging from 20 to 70 °C on the stability and activity of formate dehydrogenase, an enzyme involved in the oxidation of methanol. The activity of formate dehydrogenase increased with temperature. However, both the activity and stability declined sharply at temperatures above 60 °C. Kargi and Robinson (1982, 1984), Kargi (1987) and Brock (1978) investigated the biological oxidation of a number of RSC by pure cultures of sulphur-oxidizing microorganisms at elevated temperatures ranging from 55 to over 100 °C. The growth of these sulphur-oxidizing microorganisms at elevated temperatures was optimal at an acidic pH (1.5 to 4 with an optimum growth rate at a pH of 3) (Brock, 1978).

However, there is no information available regarding the feasibility of developing a mixed culture of microorganisms capable of biologically oxidizing both methanol and RSC at high temperatures. There is also limited information available regarding the fate and removal kinetics of these contaminants of concern in a high temperature biological treatment system. In addition, there is no information available regarding potential inhibitory effects of RSC on the growth of methanol-oxidizing microorganisms.

Furthermore, there is limited information available regarding the effect of the operating pH, on the biological removal of methanol and RSC.

This part of the study investigated the feasibility of biologically oxidizing methanol and RSC at an elevated temperature. The biotic and abiotic removal kinetics for these contaminants of concern, in a high temperature MBR, were determined. The effect of RSC on methanol removal was investigated. The feasibility of enhancing the biological removal of RSC by lowering the operating pH was also investigated.

4.2 Experimental Procedures and Equipment Set-Up

The feasibility experiment was completed in two parts. Part I investigated the feasibility of biologically removing methanol and RSC in a high temperature MBR. Part II investigated the feasibility of enhancing the biological removal of RSC by lowering the operating pH.

Part I - Feasibility of Biologically Removing Methanol and RSC in a High Temperature MBR

The primary bench scale MBR, described in Section 3.1, was used during Part I of the feasibility experiment. The MBR was fed semi-continuously with a mixture of synthetic evaporator condensate and nutrients as described in Section 3.2. The synthetic evaporator condensate contained methanol and RSC, in tap water, at concentrations similar to those observed in evaporator condensate from a local kraft pulp mill as presented in Table 4.1 and Appendix 2. The synthetic evaporator condensate did not contain hydrogen sulphide or methyl mercaptan due to the difficulty of solubilizing these RSC to specific concentrations in water. Dimethyl sulphide and dimethyl disulphide were used as surrogates for all RSC contained in the evaporator condensate. The nutrient solution contained NH_4NO_3, KH_2PO_4, $MgSO_4.7H_2O$, $MgCl.6H_2O$, $CaCl_2.7H_2O$, $FeCl_3.6H_2O$, $MnCl_2.4H_2O$, $Na_2B_4O_7.10H_2O$, $ZnSO_4.7H_2O$, $CoCl_2.6H_2O$ and

$Na_2MoO_4.2H_2O$, as required to provide non-limiting nutrient concentrations for methanol and RSC oxidizing microorganisms as presented in Appendix 3. The detailed characteristics of the synthetic evaporator condensate and nutrients are presented in Appendix 2 and 3, respectively. The operating temperature for the MBR was maintained at 55 ± 2 °C. An operating temperature of 55 °C was selected since it corresponds to the lowest expected temperature for evaporator condensate (Zuncich et al., 1993; Sebbas, 1987). Mill scale operation at a lower temperature would require cooling of the evaporator condensate before treatment and would reduce the recoverable heat content of the treated evaporator condensate. The pH was maintained above 6 (approximately 6.5) using a pH meter/controller that added sodium hydroxide as required. The aeration rate through a fine bubble diffuser was 1.6 L/minute. This produced non-limiting dissolved oxygen conditions in the MBR as discussed in Appendix A1.2.

Table 4.1

Characteristics of Synthetic Evaporator Condensate

Parameter	Real Evaporator Condensate*	Synthetic Evaporator Condensate
Methanol (mg/L)	593 ± 65	500
Hydrogen Sulphide (mg/L)	67 ± 20	-
Methyl Mercaptan (mg/L)	60 ± 27	-
Dimethyl Sulphide (mg/L)	39 ± 22	37
Dimethyl Disulphide (mg/L)	22 ± 15	25

(*measured during first monitoring period as presented in Appendix 2)

The bench scale MBR used during Part I of the feasibility experiment was operated for a 20 week period from July 1997 to December, 1997. During start-up, the MBR was inoculated with sludge from a lab scale activated sludge system treating combined kraft pulp mill effluent at 45 °C (Tai, 1998), sludge from a full scale activated sludge system treating kraft pulp mill effluent (Western Pulp Ltd. Partnership, Squamish, B.C., Canada), sludge from a pilot scale activated sludge system (UBC-Civil Engineering Pilot Plant,

Vancouver, Canada) and water and soil samples collected from Harrison Hot Springs (Harrison, B.C., Canada). Approximately 500 mL of inoculum from each location were added directly to the MBR at approximately the same time and the reactor tank was topped-off with tap water. This was repeated approximately one week following the initial inoculation. Initial steady state conditions were reached after approximately 6 weeks following the initial inoculation. Steady state conditions were assumed to have been reached when the concentration of MLVSS and the rate of methanol removal in the MBR were constant.

The removal kinetics for methanol and RSC during high temperature biological treatment were then monitored for a 14-week period following the establishment of steady state conditions. The methanol and RSC removal kinetics were determined by monitoring the concentrations of these contaminants in the MBR over time as described in Section 3.3. Samples were collected from the recycling line of the MBR and analyzed for methanol, dimethyl sulphide and dimethyl disulphide at 5, 20, 35, 50 and 65 minutes following the start of selected batch feed cycles. For some selected batch feed cycles, samples were also collected and analyzed at 80, 120 and 170 minutes following the start of the selected batch feed cycles.

Stripping of methanol and RSC from the MBR due to the aeration system was investigated following the end of Part II of the feasibility experiment. Stripping of these contaminants was investigated by measuring the changes in the concentrations of methanol and RSC in the MBR when it was filled with tap water, synthetic condensate and nutrients, and then aerated. Biological growth during the clean-water stripping tests was prevented by adding sodium azide to a concentration of 1 % (w/v) in the MBR (see Appendix A1.2).

The effect of the concentration of RSC on methanol removal was investigated by monitoring the methanol removal kinetics when the concentrations of dimethyl sulphide and dimethyl disulphide in the feed were varied. Methanol removal kinetics were monitored during selected feed cycles when dimethyl sulphide and dimethyl disulphide

were absent from the feed and when the concentrations of these RSC in the feed were doubled and quadrupled.

Part II - Feasibility of Enhancing the Biological Removal of RSC.

The secondary bench scale MBR, described in Section 3.1.1, was used during Part II of the feasibility experiment. The feed rate, operating temperature and aeration rate were similar to those used during Part I of the feasibility experiment. The operating pH was varied during Part II of the feasibility experiment. The operating pHs investigated were 6, 4 and 3. The pH was controlled using a pH meter/controller that added hydrochloric acid or potassium hydroxide as required.

The secondary bench scale MBR used during Part II of the feasibility experiment was operated over an 18 week period from Dewcember 1997 to March 1998. During start-up, the secondary MBR was inoculated with 500 mL of activated sludge from a local kraft pulp mill (Western Pulp Limited Partnership, Squamish, Canada) and with waste sludge from the MBR used in Part I of the feasibility experiment and the reactor tank was topped-off with tap water. Approximately 250 mL of waste sludge from the MBR used in Part I of the feasibility experiment were added to the secondary MBR daily over a one week period. The secondary MBR was then given sufficient time to reach steady state conditions. Steady state operating conditions were reached within approximately 3 weeks following the initial inoculation.

The effect of the operating pH on the removal kinetics for methanol and RSC during high temperature biological treatment was then monitored for a 14 week period following acclimatization. The methanol and RSC removal kinetics were determined as described in Part I of the feasibility experiment. Between each experimental run, the operating pH was decreased at a rate of 1 unit over 1 feed cycle (3 hours). Following a reduction in the operating pH from 6 to 4, steady state conditions were re-established within approximately 2 weeks. When the pH was reduced from 4 to 3, steady state conditions appeared to have been reached within 3 weeks. However, as discussed in Section 4.3.2,

the long term stability of a high temperature MBR at such a low pH was questionable. From day 1 to day 20 of the monitoring period, the operating pH was maintained at 6. On day 21, the operating pH was lowered to 4. On day 62 of the monitoring period, the operating pH was reduced to 3, where it was maintained until the end of the 14 week monitoring period. After each change in the operating pH, the MBR was re-inoculated with 100 mL of activated sludge from the Western Pulp Limited Partnership bleached kraft pulp mill. This was done to re-introduce microorganisms that might not have been able to grow under the previous growth conditions.

The methanol and RSC removal kinetics in the MBR were monitored for at least 1 sludge age, following the acclimatization period, at each operating pH investigated.

4.3 Results and Discussion

This section discusses the results obtained during the feasibility experiment. The raw data, on which this discussion is based, are presented in Appendix 4.

4.3.1 Feasibility of Biologically Removing Methanol and RSC Using a High Temperature MBR

Methanol Removal

The uptake of a single substrate, such as methanol, by a mixed culture of microorganisms can typically be modeled using the Monod-type relationship presented in Equation 4.1 (Bailey and Ollis, 1986):

$$R_{B\text{-}MeOH} = \frac{dC_{MeOH}}{dt} = U_{MeOH}\left(\frac{C_{MeOH}}{C_{MeOH} + Ks_{MeOH}}\right)\left(\frac{Ki_{MeOH}}{Ki_{MeOH} + C_{MeOH}}\right)X \qquad (4.1)$$

where $R_{B\text{-}MeOH}$ is the rate of biological removal of methanol (mg/L·minute), U_{MeOH} is the specific methanol utilization coefficient (/day), C_{MeOH} is the concentration of methanol in the MBR (mg/L), Ks_{MeOH} is the half saturation concentration (mg/L), Ki_{MeOH} is the half inhibition concentration (mg/L) and X is the concentration of MLVSS in the MBR (mg/L).

In addition to biological removal, methanol can be stripped to the atmosphere by the aeration system during biological treatment. The rate at which volatile compounds, such as methanol, are stripped due to aeration in a biological treatment system can be estimated using a first order relationship as presented in Equation 4.2 (Pitter and Chudoba, 1990):

$$R_{S-MeOH} = \frac{dC_{MeOH}}{dt} = K_{STRIP-MeOH} C_{MeOH} \tag{4.2}$$

where $R_{S\text{-}MeOH}$ is the rate of methanol removal due to stripping (mg/L·minute) and $K_{STRIP\text{-}MeOH}$ is the first order coefficient for the stripping of methanol (/minute).

Combining Equations 4.1 and 4.2 yields Equation 4.3:

$$R_{T\text{-}MeOH} = \frac{dC_{MeOH}}{dt} = U_{MEOH}\left(\frac{C_{MeOH}}{C_{MeOH} + Ks_{MeOH}}\right)\left(\frac{Ki_{MeOH}}{Ki_{MeOH} + C_{MeOH}}\right)X + K_{STRIP\text{-}MeOH} C_{MeOH} \tag{4.3}$$

where $R_{T\text{-}MeOH}$ is the total rate of methanol removal (mg/L·minute).

Equation 4.3 suggests that the rate of methanol removal is a function of the concentration of methanol remaining in an aerobic biological treatment system such as the MBR used. However, as illustrated in Figure 4.1, the observed rate of removal of methanol from the

MBR was constant with time and with the concentration of methanol remaining in the MBR over the range of concentrations examined.

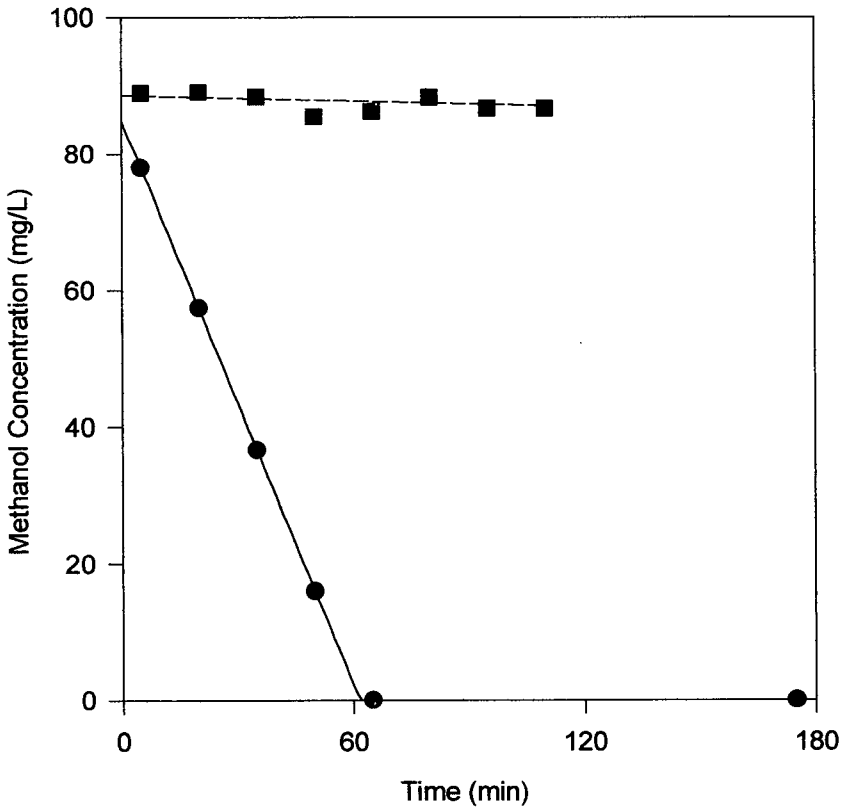


Figure 4.1 – Concentration of Methanol in MBR During a Typical Batch Feed Cycle

(●: concentration of methanol in MBR during typical biotic tests; ■: concentration of methanol in MBR during typical clean water stripping test; solid line: Equation 4.4 fitted to concentration of methanol in MBR during biotic tests ; dashed line: Equation 4.2 fitted to concentration of methanol in MBR during clean water stripping test)

The zero order removal rate indicated that the concentration of methanol in the MBR was not limiting the uptake of methanol by the mixed microbial culture in the range of concentrations examined (from approximately 100 mg/L to below detection limits of approximately 0.5 mg/L). This is similar to results reported by others for mixed cultures

of methanol-utilizing microorganisms grown at much lower temperatures. Chudoba et al. (1989) and Tai (1998) also reported rate-limiting concentrations of less than 1 mg/L for methanol at temperatures ranging from 35 to 45 °C. No studies have reported limiting methanol concentrations at higher temperatures. Kim et al. (1981) reported a half saturation concentration of 2330 mg/L (as TOC) for a mixed culture acclimatized to methanol as sole substrate at temperatures ranging from 5 to 28 °C. However, because of the variability associated with their results, their reported half saturation concentration is questionable.

The zero order removal rate also indicated that the concentration of methanol in the MBR was not inhibiting the uptake of methanol by the mixed microbial culture, even at the highest concentrations examined (up to approximately 100 mg/L). This is similar to results reported by Snedecor and Cooney (1974) for a mixed culture of methanol-utilizing bacteria grown at 51 °C. They observed that methanol was not inhibitory at concentrations below 800 mg/L. Koh et al. (1989) reported that methanol was not inhibiting at concentrations below approximately 4000 mg/L for a mixed culture acclimatized to methanol as sole substrate at a temperature of 30 °C.

In addition, the zero order removal rate indicated that stripping of methanol, due to the aeration system, did not account for a significant fraction of the methanol removed from the MBR. As presented in Equation 4.3, had stripping been significant, methanol removal would not have followed a zero order removal rate. This is consistent with the relatively low first order coefficient for the stripping of methanol estimated using clean water stripping tests. The first order coefficient for the stripping of methanol was estimated by fitting Equation 4.2 to the concentrations of methanol in the MBR measured during the clean water stripping tests (Figure 4.1). Non-linear regression, using statistical analysis software (SigmaPlot™) was used to estimate the first order coefficient for the stripping of methanol by fitting Equation 4.2 to the measured concentrations of methanol. Results from the non-linear regression are presented in Tables A4.22 to A4.24. Based on the clean water stripping tests, the first order coefficient for the stripping of methanol was estimated to be 0.00016 ± 0.00015 /minute. At this rate, stripping of methanol due to the

aeration system accounted for less than 1 % of the mass of methanol removed from the MBR. The methanol removal measured during the clean water stripping tests is presented in Figure 4.1.

For the non-limiting and non-inhibiting conditions observed, and when stripping due to the aeration system is not significant, Equation 4.3 can be simplified to a zero order relationship as presented in Equation 4.4:

$$R_{B\text{-}MeOH} = \frac{dC_{MeOH}}{dt} = U_{MeOH}X = K_{B\text{-}MeOH} \qquad (4.4)$$

where $K_{B\text{-}MeOH}$ is the zero order coefficient for the biological removal of methanol (mg/L·minute).

Equation 4.4 was fitted to the concentrations of methanol in the MBR measured during selected batch feed cycles as presented in Figure 4.1. Linear regression, using a statistical analysis package (SigmaPlot™), was used to estimate the zero order removal coefficient for the biological removal of methanol by fitting Equation 4.4 to the measured concentrations of methanol. Results from the linear regression are presented in Tables A4.2 to A4.11. The specific methanol utilization coefficient was estimated by dividing the zero order coefficient for the biological removal of methanol by the MLVSS concentration measured during the selected batch feed cycles (Table A4.1).

As illustrated in Figure 4.2, the concentration of MLVSS in the MBR varied significantly during the 14 week monitoring period. During the first four weeks, the concentration of MLVSS in the MBR appeared to have reached a steady state. After approximately 4 weeks, the operation of the MBR was disrupted due to equipment failure. This resulted in a loss of approximately half the biomass inventory in the MBR. To assist in the recovery, the MBR was immediately re-inoculated with 100 mL of activated sludge from the Western Pulp Limited Partnership bleached kraft pulp mill and topped-off with tap water. The MLVSS concentration never regained the previously observed steady state

level. However, a new steady state MLVSS concentration was reached as illustrated in Figure 4.2. The steady state MLVSS concentration measured during the second steady state period is similar to that observed during the subsequent experiments presented in Chapters 5 and 6.

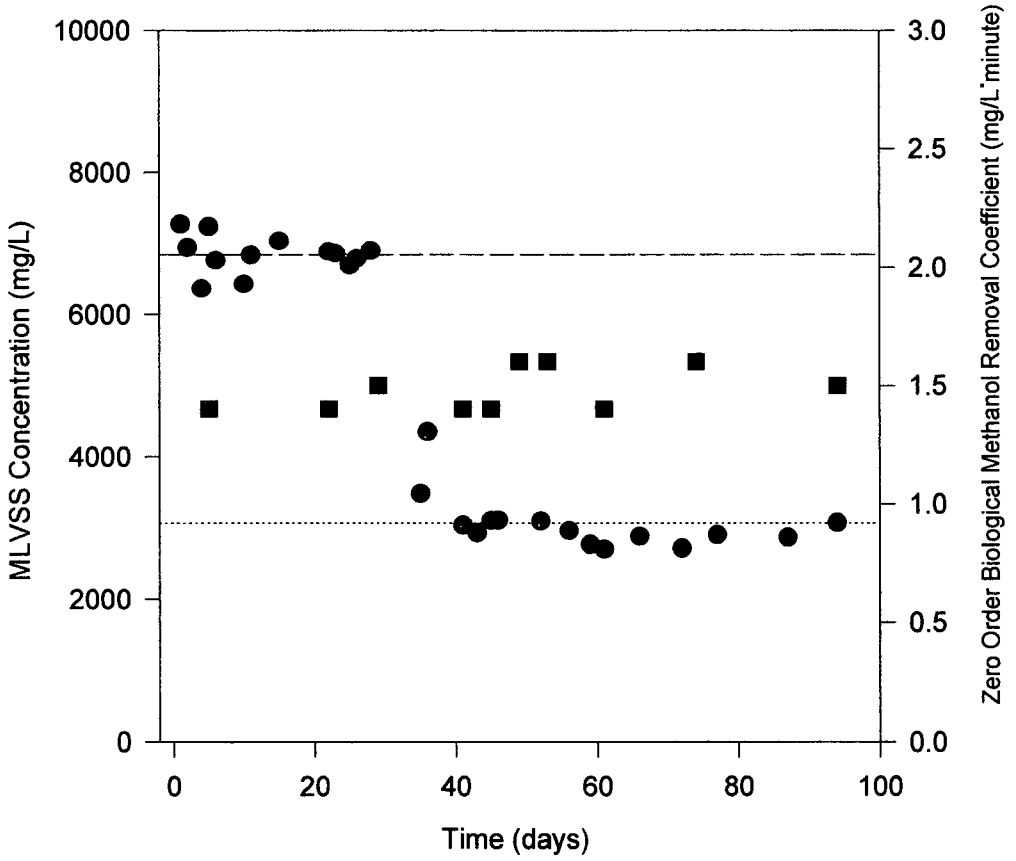


Figure 4.2 – Zero Order Coefficient for the Biological Removal of Methanol and Biomass Inventory in MBR during Monitoring Period

(●: MLVSS; ■: zero order coefficient for the biological removal of methanol; long dashed line: initial period of constant MLVSS concentration; short dashed line: final steady state period of constant MLVSS concentration)

These results suggest that during the initial period of constant MLVSS concentration, true steady state conditions had not yet been reached. During this period, the mixed liquor likely contained microorganisms, such as those present in the municipal waste sludge used to inoculate the MBR, that were not capable of growth on synthetic evaporator condensate as sole substrate. The disruption of the MBR operation due to equipment failure likely precipitated the eventual elimination of these microorganisms from the MBR. When the MBR recovered to the new steady state condition, only microorganisms that were capable of growth on synthetic evaporator condensate as sole substrate remained. The number of microorganisms present in the mixed liquor that were capable of growth on synthetic evaporator condensate was likely the same during both the first pseudo-steady state period and the second steady state period since the same amount of methanol was biologically removed in the MBR during both periods. This is also suggested by the constant zero order biological methanol removal coefficient measued during both periods, as illustrated in Figure 4.2. When the equipment failure occurred and the MLVSS concentration in the MBR was reduced by approximately 50 %, the zero order biological methanol removal coefficient would also have been expected to immediately decrease by approximately 50 % and then recover to the previously observed level. Unfortunately, the zero order biological methanol removal coefficient was not measured for 13 days following the equipment failure. It is likely that the MBR recovered and new steady state conditions were achieved within these 13 days as suggested by the constant zero order biological methanol removal coefficient and MLVSS concentration illustrated in Figure 4.2. As discussed in Chapters 5 and 6, the MBR can recover from process disruptions within 1 to 2 weeks.

The specific methanol utilization coefficient measured during the final steady state period was estimated to be 0.72 ± 0.11 /day. This specific methanol utilization coefficient was higher than those reported by others for biological systems treating evaporator condensate at a much lower temperatures. Barton et al. (1996) measured a specific methanol utilization coefficient of approximately 0.45 /day when treating real evaporator condensate in a batch activated sludge treatment system at an operating temperature of 33 ^{o}C. Therefore, it appears that the biological removal of methanol at a high temperature is

not only feasible, but that the rate of methanol removal can potentially be higher than for biological treatment systems operated at lower temperatures. This is in agreement with Lapara and Alleman (1999) who reported that in general, biological contaminant removal rates increase at higher treatment temperatures. However, as discussed in Chapter 6, the contaminants present in a real evaporator condensate matrix can affect the specific methanol utilization coefficient. Therefore, it is difficult to draw any conclusions on the effect of temperature on the specific methanol utilization coefficient at this time. In addition, the non-limiting and non-inhibiting conditions observed in the present study indicate that, with a high temperature biological treatment system, relatively high methanol removal efficiencies can be achieved for the range of methanol concentrations observed in the MBR.

Methanol removal was also not affected by the presence of dimethyl sulphide and dimethyl disulphide in the range of concentrations investigated. The concentrations of dimethyl sulphide and dimethyl disulphide in the MBR at the start of selected batch feed cycles were varied from 0 to 16 mg/L and 0 to 11 mg/L, respectively. The specific methanol utilization coefficient remained relatively constant over the range of concentrations of dimethyl sulphide and dimethyl disulphide measured in the MBR at the start of selected batch feed cycles as presented in Tables A4.2 to A4.14.

Although the pH in the MBR was kept above 6 using a pH meter/controller, the pH in the MBR tended to decrease following the start of each batch feed cycle. This was likely due to the production of CO_2 during the biological oxidation of methanol as suggested by Koh et al. (1989). This decline stopped when all of the methanol was removed from the MBR. Throughout this and subsequent experiments, the termination of the decline in the pH was used as an indicator for the complete removal of methanol from the MBR.

RSC Removal

The concentrations of dimethyl sulphide and dimethyl disulphide in the MBR were reduced from initial average concentrations of approximately 6.5 mg/L and 2.5 mg/L,

respectively, to below detection limits (approximately 0.4 mg/l), during each batch cycle as illustrated in Figure 4.3.

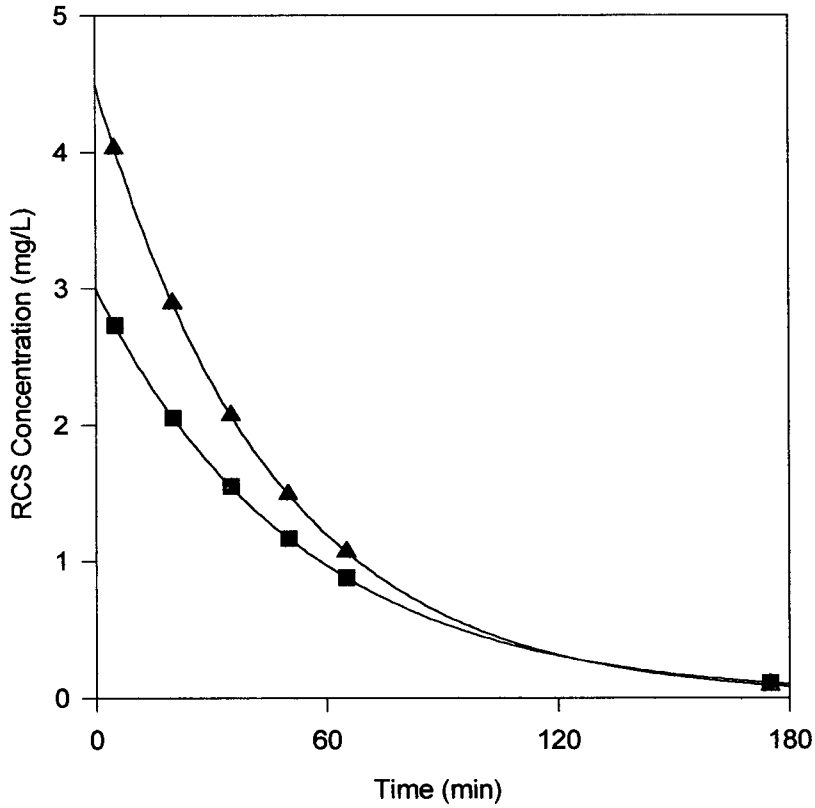


Figure 4.3 – Concentration of Dimethyl Sulphide and Dimethyl Disulphide in MBR During a Typical Batch Feed Cycle

(▲: dimethyl sulphide; ■: dimethyl disulphide; solid lines: Equation 4.5 fitted to concentrations of dimethyl sulphide and dimethyl disulphide)

The overall rates of removal for dimethyl sulphide and dimethyl disulphide were not constant with time. The concentration of RSC in the MBR measured during selected batch feed cycles followed a first order relationship as presented in Equation 4.5:

$$R_{RSC\text{-}N} = K_{RSC} C_{RSC} \quad (4.5)$$

where $R_{RSC\text{-}N}$ is the rate of removal of RSC at neutral pH(mg/L·minute), K_{RSC} is the first order coefficient for the removal of RSC (/minute) and C_{RSU} is the concentration of the RSC remaining in the MBR (mg/L).

Non-linear regression was used to fit Equation 4.5 to the RSC concentrations measured in the MBR during selected batch feed cycles. Results from the non-linear regression are presented in Tables A4.15 to A4.21. The first order coefficients for the removal of dimethyl sulphide and dimethyl disulphide were estimated to be 0.020 ± 0.0027 /minute and 0.017 ± 0.0041 /minute, respectively.

Similar first order coefficients for the removal of dimethyl sulphide and dimethyl disulphide were observed during clean water stripping tests as presented in Tables A4.15 to A4.21 and A4.25 to A4.27. This suggested that stripping due to the aeration system accounted for essentially all of the reduction in the concentrations of both dimethyl sulphide and dimethyl disulphide in the MBR.

4.3.2 Enhanced Biological Oxidation of RSC

RSC Removal

The results from Part I suggested that a mixed culture of sulphur-oxidizing microorganisms was not easily established with a mixture of nutrients and synthetic evaporator condensate as feed, in a high temperature MBR operated at a neutral pH. The observed removal of dimethyl sulphide and dimethyl disulphide from the MBR under these conditions was due predominantly to stripping by the aeration system. Although sulphur-oxidizing microorganisms that are capable of growth at elevated temperatures have been reported to grow at a relatively neutral pH, the optimal pH for their growth is

approximately 3 (Brock, 1978). To promote the growth of sulphur-oxidizing microorganisms, the operating pH in the MBR was reduced.

As illustrated in Figure 4.4, the concentrations of dimethyl sulphide and dimethyl disulphide in the MBR decreased at a faster rate when the operating pH was reduced. However, based on the clean water stripping tests, the pH did not have a significant effect on the first order coefficient for the stripping of RSC as illustrated in Figure 4.5. Therefore, the observed increase in the rate of dimethyl sulphide and dimethyl disulphide removal was assumed to be due to biological oxidation.

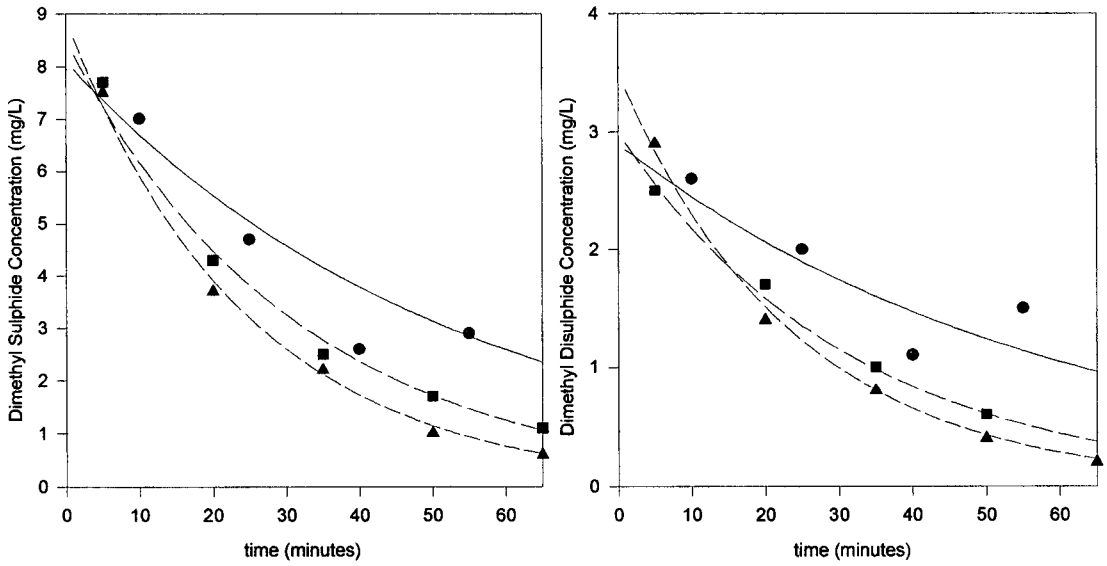


Figure 4.4 – Concentration of Dimethyl Sulphide and Dimethyl Disulphide During Typical Batch Cycles (Enhanced Biological RSC Removal)

(● and solid line: pH = 6; ▲ and long dashed line: pH = 4; ■ and short dashed line: pH = 3; lines: Equation 4.7 fitted to concentrations of dimethyl sulphide and dimethyl disulphide)

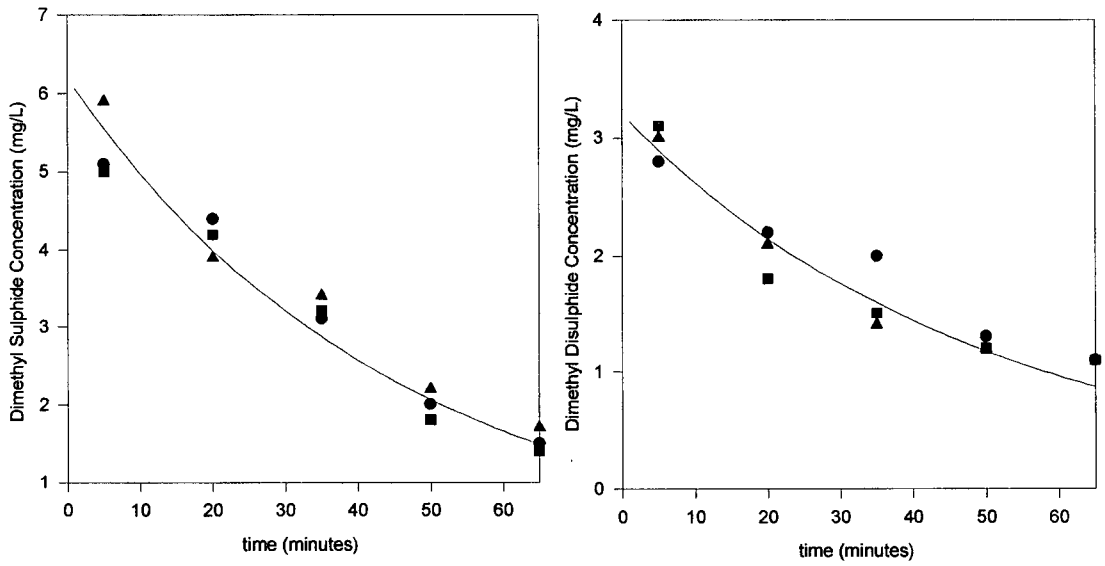


Figure 4.5 – Concentration of Dimethyl Sulphide and Dimethyl Disulphide During Typical Clean Water Stripping Tests at Different pHs

(●: pH = 6; ▲: pH = 4; ■: pH = 3; lines: Equation 4.5 fitted to concentrations of dimethyl sulphide and dimethyl disulphide)

Using the same principles as for Equation 4.3, a relationship describing the removal of RSC from a biological treatment system was developed as presented in Equation 4.6:

$$R_{T\text{-}RSC} = \frac{dC_{RSC}}{dt} = U_{RSC}\left(\frac{C_{RSC}}{C_{RSC} + Ks_{RSC}}\right)\left(\frac{Ki_{RSC}}{Ki_{RSC} + C_{RSC}}\right)X + K_{STRIP\text{-}RSC}C_{RSC} \qquad (4.6)$$

where $R_{T\text{-}RSC}$ is the total rate of RSC removal (mg/L·minute), U_{RSC} is the specific RSC utilization coefficient (/minute), Ks_{RSC} is the half saturation concentration (mg/L), Ki_{RSC} is the half inhibition concentration (mg/L) and $K_{STRIP\text{-}RSC}$ is the first order coefficient for the stripping of RSC(/minute).

Equation 4.6 suggests that the rate of RSC removal is a function of the concentration of RSC remaining in the MBR. As illustrated in Figure 4.4, the rate of dimethyl sulphide and dimethyl disulphide removal did vary as the concentration of these RSC in the MBR decreased. In fact, the rate of removal of dimethyl sulphide and dimethyl disulphide followed a first order relationship. The first order removal rates for dimethyl sulphide and dimethyl disulphide indicated that the concentrations of RSC were not inhibiting the uptake of RSC by the mixed microbial culture in the range of concentrations examined (initial concentrations up to approximately 6.5 and 2.5 mg/L for dimethyl sulphide and dimethyl disulphide, respectively, were investigated during Part II of the feasibility experiment). However, the first order removal rates for dimethyl sulphide and dimethyl disulphide indicated that the concentration of these RSC were limiting the uptake of RSC by the mixed microbial culture in the range of concentrations examined. This is consistent with results obtained by Kargi and Robinson (1982). When investigating the biological oxidation of dibenzothiophene by a pure culture of sulphur-oxidizing microorganisms, they observed a relatively high half inhibition concentration of 480 mg/L and a half saturation concentration of 666 mg/L.

For limiting and non-inhibiting conditions, Equation 4.6 can be simplified to a first order relationship as presented in Equation 4.7:

$$R_{T\text{-}RSC} = \frac{dC_{RSC}}{dt} = C_{RSC}\left(K_{B\text{-}RSC} + K_{STRIP\text{-}RSC}\right) = C_{RSC}K_{T\text{-}RSC} \qquad (4.7)$$

where $K_{B\text{-}RSC}$ is the first order coefficient for the biological removal of RSC (/minute) and $K_{T\text{-}RSC}$ is the first order coefficient for the total removal of RSC (/minute).

Equation 4.7 was fitted to the concentrations of dimethyl sulphide and dimethyl disulphide in the MBR measured during selected batch feed cycles for different operating pHs as illustrated in Figure 4.4. Non-linear regression was used to estimate the first order coefficients for the total removal of dimethyl sulphide and dimethyl disulphide. Results from the non-linear regression are presented in Tables A4.38 to A4.52. The first order

coefficients for the stripping of dimethyl sulphide and dimethyl disulphide were estimated by fitting the last term in Equation 4.6 to the concentrations of dimethyl sulphide and dimethyl disulphide in the MBR measured during the clean water stripping tests for the different operating pHs investigated (Figure 4.5). The operating pH did not significantly influence the first order coefficients for the stripping of RSC. The first order coefficients for the stripping of dimethyl sulphide and dimethyl disulphide were estimated to be 0.022 ± 0.0024 and 0.019 ± 0.0060 /minute, respectively as presented in Tables A4.53 to A4.60. The first order coefficients for the biological removal of RSC were estimated based on the difference between the first order coefficients for the total removal of RSC and the first order coefficients for the stripping of RSC measured for the different operating pHs as presented in Equation 4.7.

As illustrated in Figure 4.6, the estimated first order coefficients for the biological removal of dimethyl sulphide and dimethyl disulphide increased when the pH was reduced. The first order coefficients for the biological removal of dimethyl sulphide and dimethyl disulphide increased from essentially zero, at a pH of 6, to 0.019 ± 0.0042 /minute and 0.016 ± 0.00026 /minute, at a pH of 4, and to 0.020 ± 0.0017 /minute and 0.027 ± 0.0021 /minute, respectively, when the pH was lowered to 3. This is in agreement with Brock (1978) who reported that the optimal pH for the growth of sulphur-oxidizing bacteria capable of growth at elevated temperatures is approximately 3.

The effect of pH on biological substrate removal can be modeled using the relationship presented in Equation 4.7 (Bailey and Ollis, 1986):

$$K_{pH} = \frac{Ko_{pH}}{\left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right)} \qquad (4.8)$$

where K_{pH} is the biological removal coefficient at a given pH (/minute), Ko_{pH} is the maximum biological removal coefficient at the optimal pH (/minute), [H+] is the concentration of hydrogen ions at a given pH (mg/L) and K_1 and K_2 are dissociation constants (mg/L).

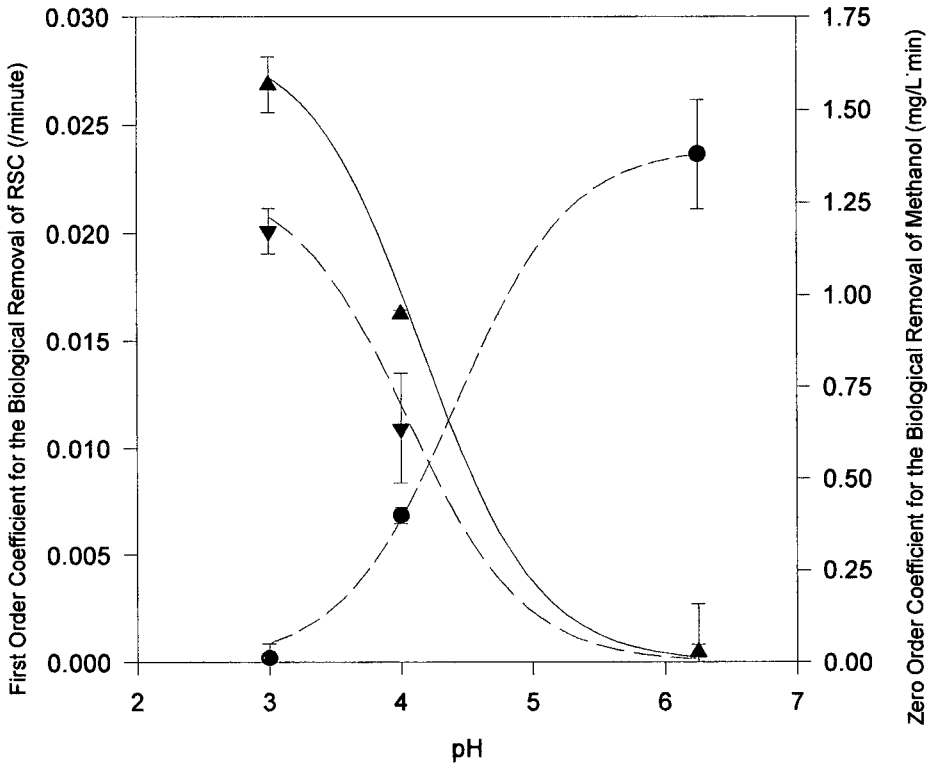


Figure 4.6 – Biological Methanol, Dimethyl Sulphide and Dimethyl Disulphide Removal Coefficients vs. Operating pH

(●: methanol; ▼: dimethyl sulphide; ▲: dimethyl disulphide; solid line: Equation 4.8 fitted to the zero order coefficient for the biological removal of methanol; long dashed line: Equation 4.8 Fitted to the first order coefficient for the biological removal of dimethyl sulphide; short dashed line: Equation 4.8 Fitted to the first order coefficient for the biological removal of dimethyl disulphide; error bars represent 90 % confidence interval of measurements made)

Equation 4.8 was successfully fitted to the estimated first order coefficients for the biological removal of RSC using non-linear regression (Figure 4.6). As illustrated in Figure 4.6, the biological removal of both dimethyl sulphide and dimethyl disulphide was significantly inhibited at a pH above approximately 4.5.

The results from Part II of the feasibility experiment indicate that it is possible to increase the rate of biological RSC removal. However, even under optimal conditions for the biological oxidation of RSC, stripping still due to the aeration system accounted for approximately 50 % of the RSC removed from the MBR. Also, the stability of a high temperature MBR operated at a low pH is questionable. As illustrated in Figure 4.7, after approximately 4 weeks of operation at a pH of 3, the total first order coefficient for the removal of dimethyl sulphide and dimethyl disulphide declined sharply. After five weeks of operation at a pH of 3, there was no significant biological removal of RSC.

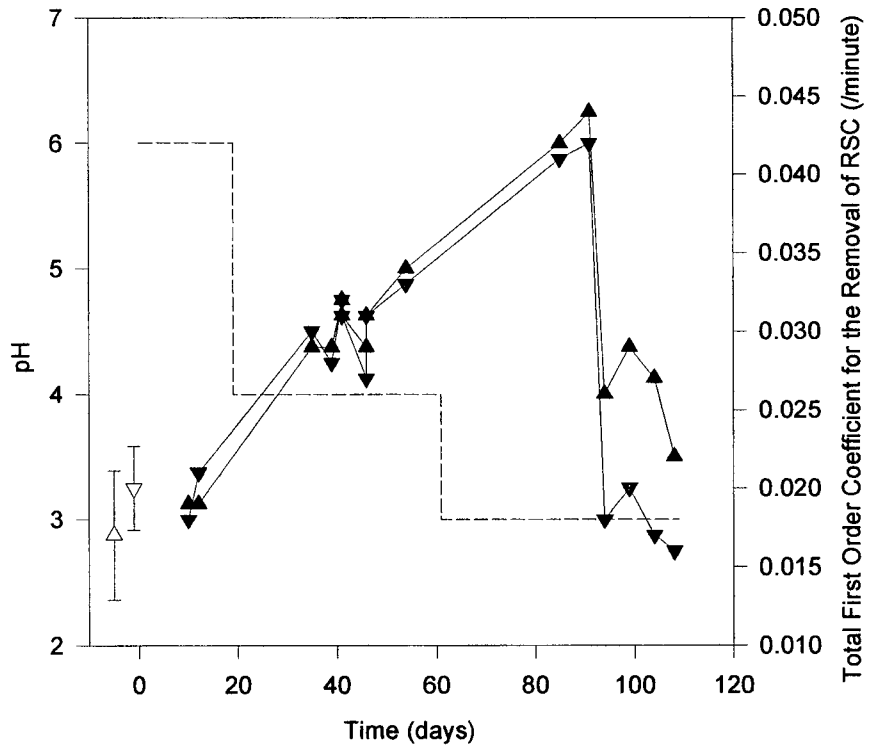


Figure 4.7 – Effect of pH on Total First Order Coefficient for the Removal of RCS During Monitoring Period

(▼: dimethyl sulphide; ▲: dimethyl disulphide; dashed line: operating pH; clear symbols are averages from Part I of feasibility experiment (i.e., due to stripping by the aeration system only))

As an alternative to the biological oxidation of the RSC contained in the evaporator condensate, the off-gas from a high temperature biological treatment system could be treated using a designated catalytic incinerator or a biofilter. The off-gas could also be hard piped to an existing power or recovery boiler for incineration. The incineration of RSC in the power or recovery boiler could also potentially reduce the overall dioxin emissions from a kraft pulp mill (Uloth, 1999).

Methanol Removal

Although it was possible to increase the first order coefficient for the biological removal of RSC by decreasing the pH, the zero order coefficient for the biological removal of methanol was significantly reduced when the pH was lowered as illustrated in Figure 4.6. The zero order coefficient for the biological removal of methanol was estimated by fitting Equation 4.4 to the concentrations of methanol in the MBR measured during selected batch feed cycles for different operating pHs using linear regression. The estimated first order coefficients for the biological removal of methanol were 1.38 ± 0.24 and 0.4 ± 0.034 for an operating pH of 6 and 4, respectively. At a pH of 3, there was essentially no biological removal of methanol.

Equation 4.8 was successfully fitted to the estimated zero order coefficients for the biological removal of methanol using non-linear regression (Figure 4.6). As illustrated in Figure 4.6, the zero order coefficient for the biological removal of methanol was significantly reduced at a pH below approximately 4.5. At a pH of 3, there was no significant biological removal of methanol. Kim and Armstrong (1981) observed a similar reduction in the methanol removal rate when they investigated the effects of pH on a mixed microbial culture. The reduction in the zero order biological methanol removal coefficient at a lower pH is likely due to the instability of formate dehydrogenase, an enzyme involved in the biological oxidation of methanol, at a pH below 6 (Izumi et al., 1989). Formate dehydrogensase has been reported to be an extracellular enzyme and would therefore be impacted by the pH of the mixed liquor

(Jensen and Corpe, 1991). However, further research would be required to confirm this hypothesis.

4.4 Summary

The biological removal of methanol from synthetic evaporator condensate using a high temperature MBR was determined to be feasible. The preliminary results suggested that the specific methanol utilization coefficient was higher in a high temperature biological treatment using an MBR than in a conventional biological treatment system operated at a lower temperature.

Simultaneous biological removal of methanol and RSC from synthetic evaporator condensate using a high temperature MBR was not feasible. A low operating pH was required for biological oxidation of RSC to occur at an elevated temperature. Consequently, a two stage system, with one stage operating at a neutral pH and the other operating at an acidic pH, would be required to biologically remove both methanol and RSC. This would significantly add to the cost of a biological system to treat condensate for reuse. Even at an optimal pH for the growth of sulphur-oxidizing microorganisms, stripping due to the aeration system accounted for approximately 50 % of the RSC removed from the MBR. The results also indicated that the stability of a mixed microbial culture at a low pH is questionable. In addition, biological removal of methanol was significantly inhibited at the pH required for biological RSC removal to occur. For these reasons, the biological oxidation of RSC in a high temperature MBR was not considered to be feasible and the simultaneous biological removal of methanol and RSC was not further investigated.

Chapter 5 – Effect of Operating Temperature on the Biological Removal of Methanol

5.1 Introduction

The results from the feasibility experiment presented in Chapter 4 indicated that it was possible to biologically remove methanol from synthetic evaporator condensate at a temperature of 55 °C. However, the operating temperature selected for the feasibility study corresponded to the lower end of the expected range of temperatures for evaporator condensate. Reported temperatures for evaporator condensate range from 55 to 70 °C (Zuncich et al., 1993; Sebbas, 1987). Knowledge of the effect of the operating temperature over the entire temperature range is required to properly understand, design and operate a biological treatment system for the treatment of evaporator condensate for reuse.

There is limited information available regarding the effect of elevated temperatures on a mixed culture of methanol-consuming microorganisms. Snedecore and Cooney (1974) investigated the observed growth yield for a mixed culture of methanol-consuming microorganisms at temperatures ranging from 45 to 65 °C. They observed an increase in the observed growth yield with temperature, to a maximum at approximately 58 °C. Above 58 °C, the observed growth yield declined. Izumi et al. (1989) investigated the activity and stability of formate dehydrogenase, an enzyme involved in the oxidation of methanol, at temperatures ranging from 20 to 70 °C. They observed an increase in the activity with temperature to a maximum at approximately 55 °C. Above 60 °C, both the activity and the stability of formate dehydrogenase declined rapidly. There is no reported information on the effect of elevated temperatures on methanol removal kinetics for a mixed culture of microorganisms.

This part of the study investigated the effects of the operating temperature on methanol removal by a mixed culture of microorganisms over the reported temperature range for

evaporator condensate. The effects of elevated temperatures on the specific methanol utilization coefficient, the specific growth coefficient, the observed growth yield and the metabolism of methanol were determined.

5.2 Experimental Procedures and Equipment Set-up

The effect of elevated operating temperatures on a mixed culture of methanol-consuming microorganisms was investigated in two Parts. Part I investigated the effect of elevated operating temperatures on methanol removal kinetics (specific utilization coefficient, specific growth coefficient, observed growth yield). Part II investigated the effect of the rate of temperature increase, the initial acclimatization temperature and the source of the inoculum on methanol removal kinetics. The effect of elevated temperatures on the metabolism of methanol was also investigated in Part II.

Part I – Effect of Elevated Operating Temperatures on Methanol Removal Kinetics

The primary bench scale MBR, described in Section 3.1, was used during Part I. The MBR was fed semi-continuously with a mixture of synthetic evaporator condensate and nutrients.

As discussed in Section 2.3.4, the permeate flux through a membrane decreases with time. To prevent the reactor from overflowing, the permeate flux must be kept greater than the influent flow rate. A relatively high permeate flux was maintained throughout his study by periodically cleaning the membrane component of the MBR, as discussed in Appendix 9. To reduce the frequency at which the membrane component of the MBR had to be cleaned, to increase the permeate flux through the membrane, the flow rate to the MBR was decreased by 75 %. To maintain an equivalent contaminant loading rate to that used during the feasibility experiment (Chapter 4), the concentrations of the contaminants in the synthetic evaporator condensate were increased four fold. The

aeration rate used was 1.6 L/minute. This provided non-limiting dissolved oxygen conditions in the MBR as discussed in Appendix A1.2.

The removal kinetics for methanol (specific methanol utilization coefficient, specific growth coefficient and observed growth yield) during high temperature biological treatment were monitored over a 16 week period from January, 1998, to May, 1998. The methanol removal kinetics were determined as described in Section 3.3. Samples were collected from the recycling line of the MBR and analyzed for methanol at 5, 20, 35, 50 and 65 minutes following the start of selected batch feed cycles. The mixed culture developed during Part I of the feasibility study was used. The effects of high temperature on methanol removal kinetics were investigated by monitoring the rate of methanol removal in the MBR at operating temperatures of 55, 60, 65 and 70 °C. The upper temperature limit of 70 °C corresponded to the maximum expected temperature for condensate. The lower temperature limit of 55 °C represented an operating temperature below which pre-cooling of the condensate was thought to be required. Between each experimental run, the operating temperature was increased by 5 °C over one feed cycle (3 hours). A relatively large step change in the operating temperature was selected to investigate the effect of relatively large temperature variations on the performance of the MBR to treat evaporator condensate for reuse. Relatively large step changes in the temperature of the evaporator condensate could be caused by process changes or upsets in the pulp mill. After each temperature change, it was noted that steady state operating conditions were re-established within approximately 1 week (Figure 5.4). The operating temperature was set to 55 °C from January 12, 1998 and increased to 60, 65 and 70 °C on January 28, 1998, March 4, 1998 and April 1, 1998, respectively. The MBR was shut down on April 30, 1998.

Following the completion of Part I, the biomass in the MBR was inactivated by the addition of sodium azide as described in Appendix A1.2. The abiotic methanol removal rates were then determined for operating temperatures of 55, 60, 65 and 70 °C.

Part II – Effect of Rate of Temperature Increase, the Acclimatization Temperature and the Source of the Inoculum on Methanol Removal Kinetics

The bench scale MBR used in Part II was operated over a 12 week period from October, 1998 to January, 1999. The configuration (primary MBR) and operation (aeration and feed composition) of the MBR was as described for Part I.

The bench scale MBR was inoculated with 2 liters of waste sludge from one source only (full scale activated sludge system treating combined kraft pulp mill effluent - Western Pulp Ltd. Partnership, Squamish, B.C.,Canada). This was repeated approximately one week following the initial inoculation. The operating temperature in the MBR was set to 60 ± 2 °C during the acclimatization period. The acclimatization temperature of 60 °C corresponded to the optimal operating temperature observed during Part I. Steady state conditions were reached after approximately 6 weeks of acclimatization.

The effects of high operating temperature on methanol removal kinetics were again investigated by monitoring the rate of methanol removal in the MBR at operating temperatures of 60 and 65 °C as described in Section 3.3. Samples were collected from the ultrafiltration cartridge effluent line and analyzed for methanol at 15, 30, 45, 60 and 75 minutes following the start of selected batch feed cycles. The first sample was collected 15 minutes following the start of selected batch feed cycles to minimize the dilution effect that can occur in the membrane casing. For some selected batch feed cycles, samples were also collected and analyzed at 90 minutes following the start of the selected batch feed cycles. Operation at these temperatures was re-investigated since most of the changes in the methanol removal kinetics measured during Part I, were observed to occur in this temperature range. In Part II, the change in operating temperature was made at a much slower rate to minimize the temperature shock to the mixed microbial culture. The operating temperature of the MBR was increased from 60 to 65 °C by 1 °C every 4 days. This was equivalent to a 5 °C temperature increase over one sludge age. The operating temperature was set to 60 °C from October 10, 1998 to October 18, 1998. The temperature was then increased to 61, 62, 63, 64 and 65 °C on

October 18, 1998, October 22, 1998, October 26, 1998, October 30, 1998 and December 4, 1998, respectively. The reactor was shut down on January 12, 1999.

Part II also investigated the effect of the operating temperature on the metabolism of methanol. Off-line batch degradation tests using radio-labeled methanol were completed as described in Appendix A1.3.2. These tests determined what fraction of the methanol consumed by the mixed microbial culture was incorporated into biomass and what fraction was completely oxidized to CO_2, at operating temperatures of 55, 60 and 65 °C. For the operating temperatures of 60 and 65 °C, the off-line batch degradation tests were completed using acclimatized biomass obtained from the MBR during Part II of the present experiment. For the operating temperature of 55 °C, the off-line tests were done using biomass from the secondary bench scale MBR, described in Section 3.1, operated at a temperature of 55 °C. The secondary MBR was inoculated and acclimatized as described above.

In both parts of the study, the mixed microbial community present in the MBR was qualitatively examined as described in Appendix A1.2.

5.3 Results and Discussion

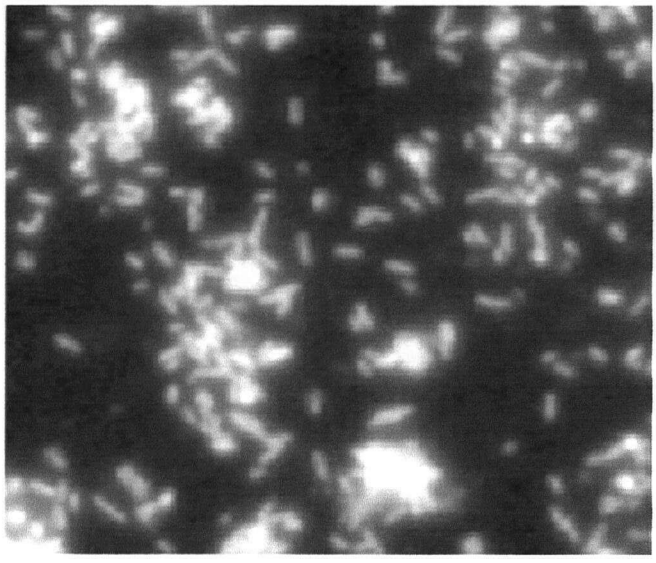
This section discusses the results obtained during the second experiment investigating the effect of high temperature operation on the biological removal of methanol from synthetic evaporator condensate. The raw data on which the discussion is based are presented in Appendix 5.

5.3.1 Mixed Culture of Methanol-Consuming Microorganisms

At all operating temperatures investigated, it was possible to grow a mixed culture of methanol-consuming microorganisms. From the qualitative microbial examination

following acridine orange staining, the microbial community appeared to consist exclusively of 0.5 μm to 1 μm, by 5 μm to 7.5 μm, rod-shaped microorganisms as illustrated in Picture 5.1.

In the present experiment, similar microbial communities and similar methanol removal kinetics were observed during both Parts I and II. This indicates that a mixed microbial culture capable of consuming methanol can easily be established in an MBR with sludge obtained from a combined mill effluent biological treatment system alone. It also indicates that a mixed microbial culture can be acclimatized directly at the optimal operating temperature of 60 °C.



Picture 5.1 – Qualitative Examination of Microbial Community in MBR

As discussed in Section 5.3.3, the maximum specific methanol utilization coefficient and the maximum specific growth coefficient were observed to occur at an operating temperature of approximately 60 °C. This indicates that the mixed culture predominantly consisted of thermophilic microorganisms. By definition, thermophilic microorganisms thrive at temperatures greater than approximately 45 to 50 °C (Brock et al., 1994).

5.3.2 Effect of the Operating Temperature on the Biological Removal of Methanol

Abiotic Removal of Methanol

As illustrated in Figure 5.1, the operating temperature exerted a substantial effect on the abiotic removal of methanol from the MBR. Abiotic removal was investigated by monitoring the concentration of methanol in the MBR when the biomass was inactivated by adding sodium azide to the mixed liquor. Abiotic methanol removal was observed to follow a first order relationship. The first order coefficient for the abiotic removal of methanol was estimated by fitting a first order equation, similar to that presented in Equation 4.2, to the concentrations of methanol in the MBR measured during abiotic tests (Figure 5.1). Non-linear regression was used to estimate the first order methanol removal coefficients for the different operating temperatures investigated. Results from the non-linear regression are presented in Tables A5.33 to A5.40.

The first order coefficient for the abiotic removal of methanol measured at a temperature of 55 °C was similar to the first order coefficient for the stripping of methanol measured during the feasibility experiment using clean water (Chapter 4). This indicated that stripping, due to the aeration system in the MBR, was responsible for the observed abiotic removal of methanol. The first order coefficient for the abiotic removal of methanol, hereafter referred to as the first order coefficient for the stripping of methanol, increased significantly when the operating temperature was increased as illustrated in Figure 5.2. The first order coefficient was observed to follow a power law relationship (linear relationship on a semi-log scale) with respect to the temperature. This is consistent with results by Blackwell et al. (1982) who reported a power law relationship between the tendency of a compound to volatilize (i.e. Henry's law constant) and the temperature of a solution containing the volatile compound. The first order coefficients for the stripping of methanol were estimated to be 0.00021 ± 0.000011, 0.00024 ± 0.000046, 0.00032 ± 0.000035 and 0.0004 ± 0.000046 mg/L·minute, respectively, for operating temperatures of 55, 60, 65 and 70 °C.

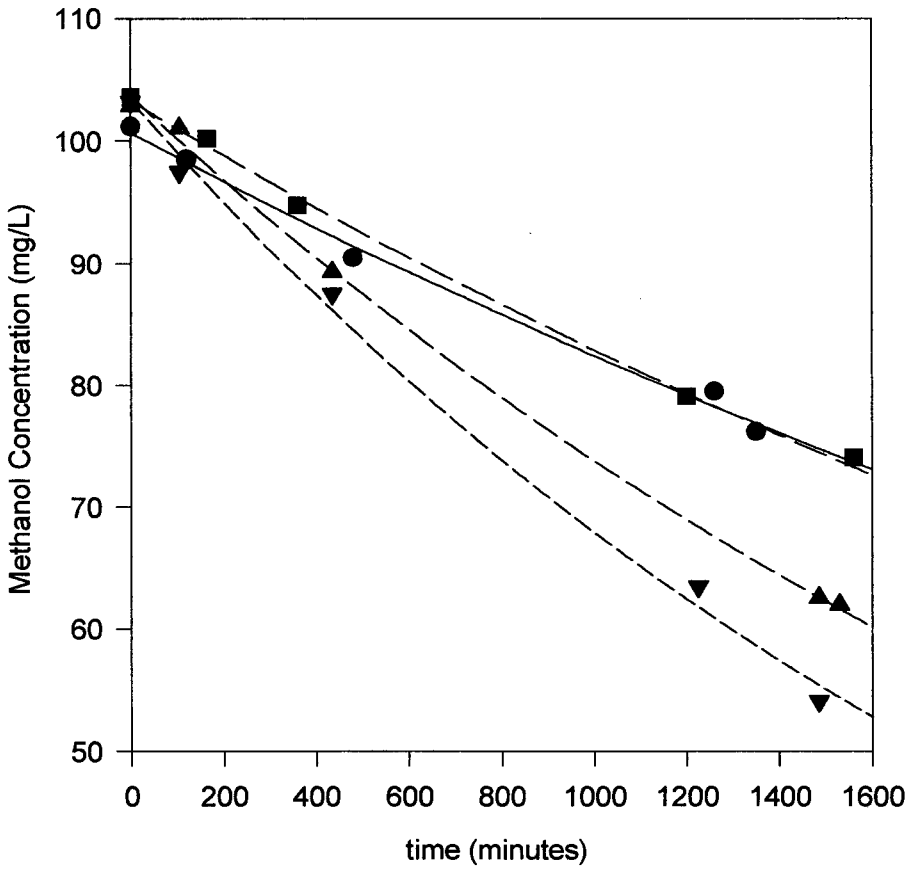


Figure 5.1 – Concentration of Methanol in MBR During Typical Batch Feed Cycles with Inactivated Biomass for Each of the Operating Temperatures Investigated (● and solid line: 55 °C;■ and long dashed line: 60 °C; ▲ and medium dashed line: 65 °C; ▼ and short dashed line: 70 °C; lines: Equation 4.4 fitted to the measured methanol concentrations)

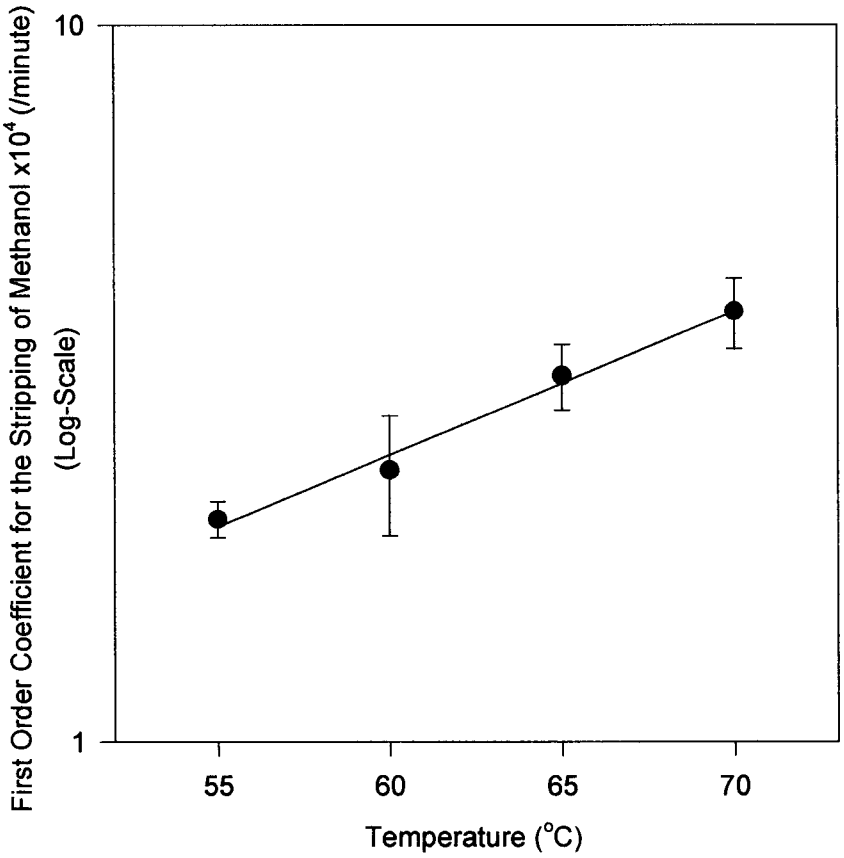


Figure 5.2 – First Order Coefficient for the Stripping of Methanol vs. Operating Temperature (tests done with inactivated biomass)

(error bars represent 90 % confidence interval)

Overall Removal of Methanol

As observed during the feasibility experiment (Chapter 4), the overall rate of removal of methanol in the MBR was again observed to be constant with time and with the concentration of methanol remaining in the MBR for all operating temperatures investigated. Figure 5.3 illustrates the concentration of methanol in the MBR for selected batch feed cycles, for each of the operating temperatures investigated.

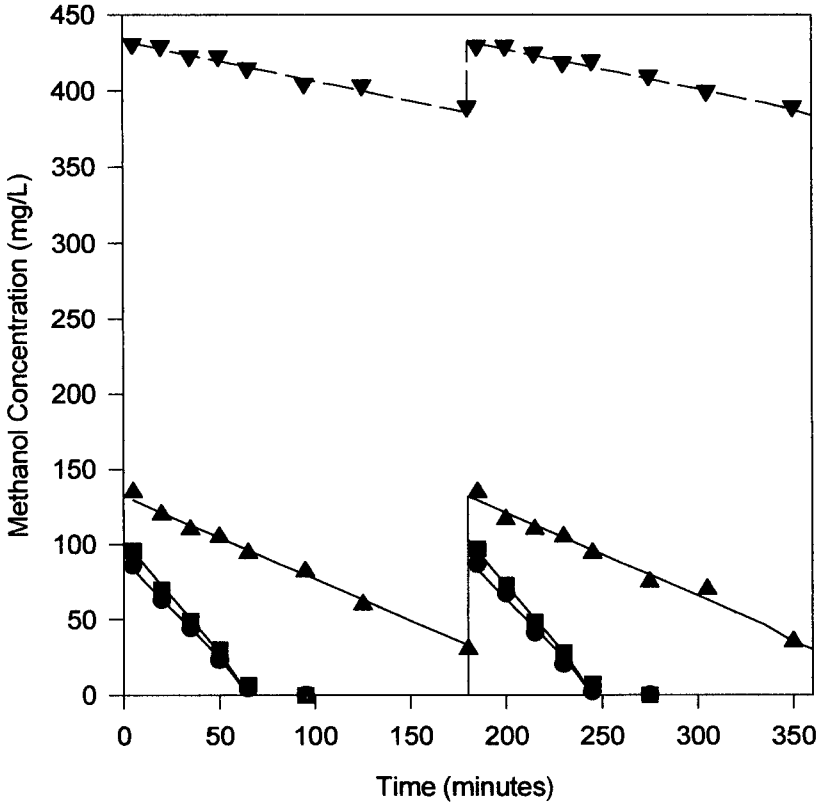


Figure 5.3 – Concentration of Methanol in MBR During Two Typical Batch Feed Cycles for Each of the Operating Temperatures Investigated

(●: 55 °C; ■: 60 °C; ▲: 65 °C; ▼: 70 °C; solid lines: Equation 4.4 fitted to measured methanol concentrations; dashed line: Equation 5.1 fitted to measured methanol concentrations)

At operating temperatures of 55 and 60 °C, the concentration of methanol in the MBR was reduced from initial values of approximately 100 mg/L to less than 0.5 mg/L (method detection limit) before the end of each batch cycle. The lower methanol removal rates at operating temperatures of 65 and 70 °C resulted in the presence of residual amounts of methanol in the MBR at the end of each batch feed cycle, which in turn, resulted in a higher concentration of methanol in the MBR at the start of the following batch feed cycle.

As previously discussed (Chapter 4), the zero order methanol removal rate in the MBR indicated that the concentration of methanol in the MBR was not limiting or inhibiting the uptake of methanol by a mixed microbial culture over the range of concentrations examined, for all operating temperatures investigated. Muck and Grady (1974) reviewed the results from a number of studies investigating the effect of temperature on half saturation concentrations. Their review indicated that the half saturation concentration could either increase or decrease with increasing temperature, depending on the microorganisms and the growth conditions. Unfortunately, it was not possible to investigate the effect of temperature on the half inhibition concentration or the half saturation concentration based on the data collected.

Stripping due to the aeration system did not substantially contribute to the overall rate of methanol removal for operating temperatures of 55, 60 and 65 °C. The fraction of methanol that was stripped from the MBR due to the aeration system was estimated by using the first order stripping coefficients and the overall methanol removal rates for the different operating temperatures investigated. Stripping accounted for approximately 1, 1 and 5 % of the mass of methanol removed from the MBR for operating temperatures of 55, 60 and 65 °C, respectively. However, for an operating temperature of 70 °C, stripping accounted for approximately 53 % of the mass of methanol removed from the MBR.

Equation 4.4, was fitted to the concentrations of methanol in the MBR measured during the selected batch feed cycles for operating temperatures of 55, 60 and 65 °C (Figure 5.3). Linear regression was used to estimate the zero order coefficients for the biological removal of methanol for each operating temperature investigated. Results from the linear regression are presented in Tables A5.1 to A5.22, and Tables A5.45 to A5.57 for Parts I and II of the present experiment, respectively.

For an operating temperature of 70 °C, where stripping accounted for a significant fraction of the methanol removed, the last term of Equation 4.3 was added to Equation 4.4 as presented in Equation 5.1:

$$R_{T\text{-}MeOH} = \frac{dC_{MeOH}}{dt} = K_{B\text{-}MeOH} + K_{STRIP\text{-}MeOH} C_{MeOH} \quad (5.1)$$

Equation 5.1 was fitted to the concentrations of methanol in the MBR measured during the selected batch feed cycles for an operating temperature of 70 °C (Figure 5.3). Non-linear regression was used to estimate the zero order coefficient for the biological removal of methanol at an operating temperature of 70 °C. Results from the non-linear regression are presented in Tables A5.23 to A5.32.

As illustrated in Figure 5.4, the operating temperature had a significant effect on the zero order coefficients for the biological removal of methanol. When the operating temperature was increased from 55 to 60 °C, the zero order coefficient for the biological removal of methanol initially declined immediately, as illustrated in Figure 5.4. The decline was followed by a relatively rapid recovery. After approximately one week following the temperature increase, the zero order coefficient for the biological removal of methanol had reached a new steady state value that was higher than that observed at an operating temperature of 55 °C. When the operating temperature was increased from 60 to 65 °C, the zero order coefficient for the biological removal of methanol again initially declined immediately. As with the temperature increase from 55 to 60 °C, the decline was followed by a rapid recovery. However, the recovery was not as substantial and the new steady state zero order coefficient for the biological removal of methanol was lower than that observed at an operating temperature of 60 °C. When the operating temperature was increased from 65 to 70 °C, the zero order coefficient for the biological removal of methanol once again declined immediately. However, no recovery occurred following the decline. The new steady state zero order coefficient for the biological removal of methanol at 70 °C was lower than that observed at an operating temperature of 65 °C.

The estimated steady state zero order coefficients for the biological removal of methanol were 1.14 ± .049, 1.40 ± 0.13, 0.61 ± 0.07 and 0.12 ± 0.067 mg/L·minute, for operating temperatures of 55, 60, 65 and 70 °C, respectively.

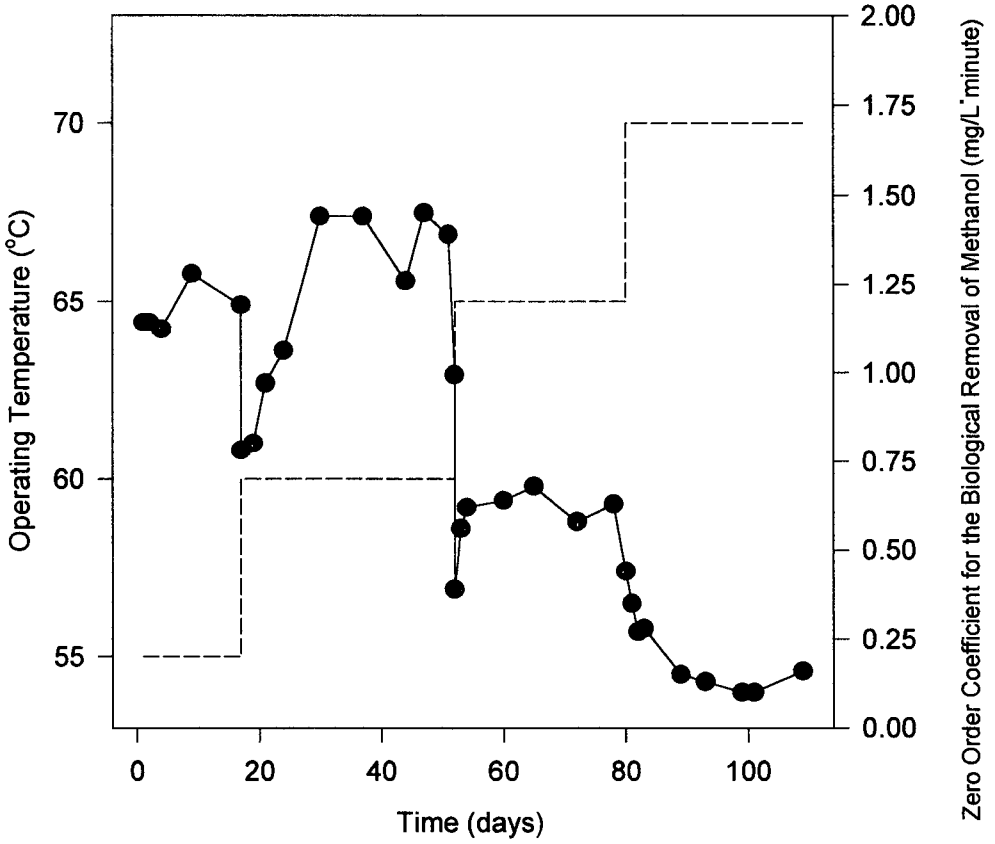


Figure 5.4 – Effect of Operating Temperature on the Zero Order Coefficient for the Biological Removal of Methanol During Part I

(●: zero order methanol removal constant; dashed line: operating temperature)

Although the values of the steady state zero order coefficients for the biological removal of methanol estimated during Parts I and II were relatively similar, the pattern of adaptation to the temperature increases was different when the operating temperature was increased at a slower rate, as illustrated in Figures 5.4 and 5.5. When the operating temperature was increased above 60 °C, at a rate of 1 °C every 4 days, the zero order coefficient for the biological removal of methanol declined, but not as substantially as observed when the temperature was increased at a rate of 5 °C over 1 batch feed cycle. A relatively constant zero order coefficient for the biological removal of methanol was observed throughout the period when the operating temperature was increased. After one

to two weeks of operation at 65 °C, the zero order coefficient for the biological removal of methanol declined to a steady state level similar to that observed during Part I.

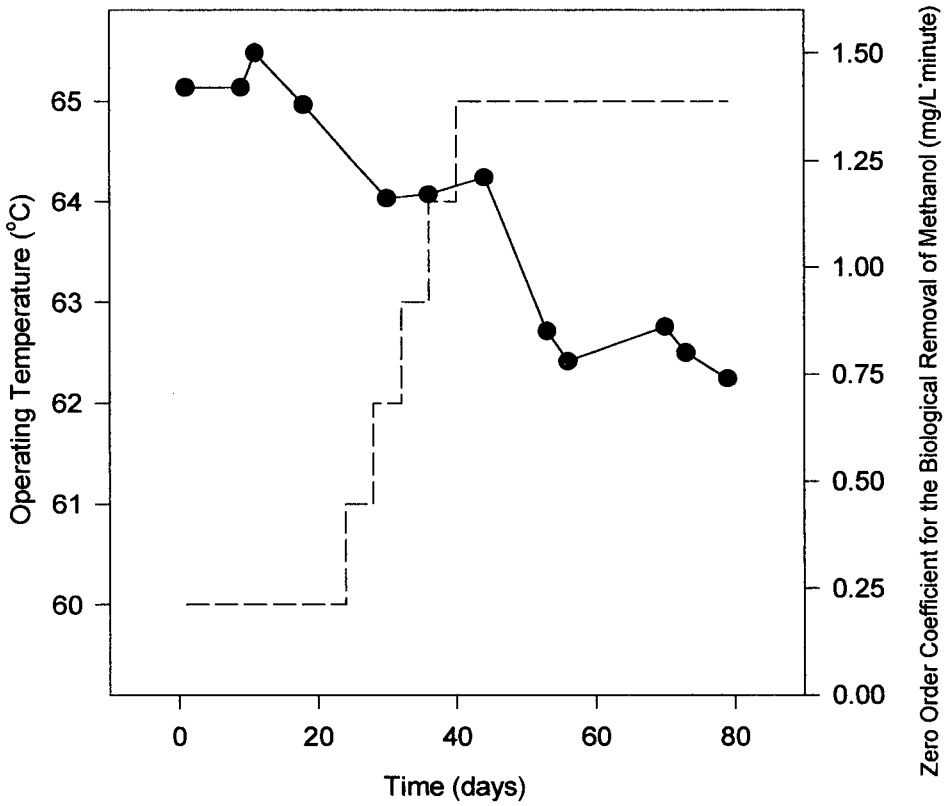


Figure 5.5 – Effect of Operating Temperature on the Zero Order Coefficient for the Biological Removal of Methanol During Part II

(●: zero order methanol removal constant; dashed line: operating temperature)

These results indicated that the zero order coefficient for the biological removal of methanol was substantially affected by relatively large instantaneous temperature changes. However, the zero order coefficient for the biological removal of methanol was not substantially affected by temperature changes in the order of 1 °C. The mixed culture appeared to have the ability to tolerate slow temperature changes over short periods of time. Therefore, variations in the operating temperature in the MBR should be kept to a minimum. These results also indicated that the long-term steady state zero order coefficient observed for the biological removal of methanol is relatively similar, regardless of the rate at which the desired temperature is reached.

5.3.3 Determination of the Optimal Operating Temperature for the Biological Removal of Methanol

The growth rate for a mixed culture of methanol-consuming microorganisms can be related to the rate of methanol consumed as presented in Equation 5.2:

$$R_G = YR_{B\text{-}MeOH} \qquad (5.2)$$

where R_G is the rate of microbial growth (mg/L·day) and Y is the observed microbial growth yield (mg biomass produced per mg methanol consumed).

Substituting $R_{B\text{-}MeOH}$ from Equation 4.4 into 5.2 and rearranging produces Equation 5.3:

$$\mu = YU_{MeOH} \qquad (5.3)$$

where μ is the specific growth coefficient (/day).

The effect of temperature on the specific growth coefficient can typically be described by the Arrhenius relationship as presented in Equation 5.4 (Bailey and Ollis, 1986):

$$\mu_T = Ae^{\frac{-E}{RT}} \qquad (5.4)$$

where μ_T is the specific growth coefficient at operating temperature T (/day), E is the Arrhenius activation energy for the growth-limiting reaction (J/mole), R is the universal gas constant (8.314 J/K·mole), T is the absolute operating temperature (K) and A is an Arrhenius activation constant (/day). This relationship assumes that the growth-limiting step for the mixed microbial culture is the same at all temperatures, and that only one enzyme is involved in the growth-limiting step (Bailey and Ollis, 1986).

For wastewater treatment applications, Equation 5.4 is typically simplified and approximated as presented in Equation 5.5:

$$\mu_{T'} = \mu_D \theta^{(T' - T'_D)} \qquad (5.5)$$

where $\mu_{T'}$ is the specific growth coefficient at operating temperature T' (/day), μ_D is the specific growth coefficient at operating temperature T'_D (/day), θ is the temperature activation coefficient, subscript D refers to the datum operating temperature and T' is the operating temperature (°C).

This simplified version of the Arrhenius relationship is commonly used to model the effect of temperature on biological removal kinetics in wastewater treatment systems (Metcalf and Eddy, 1991). The approximation is accurate over temperature ranges typically encountered in biological treatment systems.

As illustrated in Figure 5.6, slight increases in the specific methanol utilization coefficient and the specific growth coefficient were observed when the operating temperature was increased from 55 to 60 °C, as suggested by the relationships presented in Equations 5.4 and 5.5. The specific methanol utilization coefficients were estimated by dividing the zero order biological methanol removal coefficients by the MLVSS concentrations measured during the selected feed cycles for the different operating temperatures. The MLVSS concentrations measured for the different operating temperatures are presented in Tables A5.41 to A5.44 and Tables A5.58 and A5.59 for Parts I and II, respectively. The specific growth coefficients were estimated by multiplying the specific methanol utilization coefficients by the observed growth yield. The observed growth yields, for the different operating temperatures investigated, are presented in Tables A5.41 to A5.44 and Tables A5.58 and A5.59 for Parts I and II, respectively.

Above an operating temperature of 60 °C, both the specific methanol utilization coefficient and the specific growth coefficient declined sharply as illustrated in Figure 5.6. This is in contradiction to the relationships presented in Equations 5.4 and 5.5. These relationships suggest that the specific growth coefficient should continuously increase as the temperature increases. A maximum specific methanol utilization

coefficient and a maximum specific growth coefficient of 0.84 ± 0.08 /day and 0.11 ± 0.011 /day, respectively, were estimated at an operating temperature of approximately 60 °C. Above a critical temperature there is a significant reduction in the active fraction of the growth-limiting enzyme in a microbial culture, resulting in an overall decline in specific growth coefficient (Bailey and Ollis, 1986). Equations 5.4 and 5.5 do not account for the inactivating effect of temperature on the growth-limiting enzyme. Models based on these equations can therefore significantly overestimate contaminant removal rates at elevated temperatures.

Below the sterilization temperature (i.e. temperature above which non-reversible inactivation occurs), the active and inactive fractions of a growth-limiting enzyme can be estimated from an Arrhenius-type relationship as presented in Equation 5.6 (Bailey and Ollis, 1986):

$$f_I = f_A B e^{\frac{-E'}{RT}} \tag{5.6}$$

where f_A is the active fraction of the growth-limiting enzyme, f_I is the inactive fraction of the growth-limiting enzyme, the sum of $f_A + f_I$ equals 1, E' is the Arrhenius inactivation energy for the inactivation of the growth-limiting reaction (J/mole) and B is an Arrhenius inactivation constant (-).

Combining Equations 5.4 and 5.6 yields Equation 5.7:

$$\mu_T = A e^{\frac{-E}{RT}} \left(\frac{1}{1 + B e^{\frac{-E'}{RT}}} \right) \tag{5.7}$$

where the term in parentheses corresponds to the active fraction of the growth-limiting enzyme.

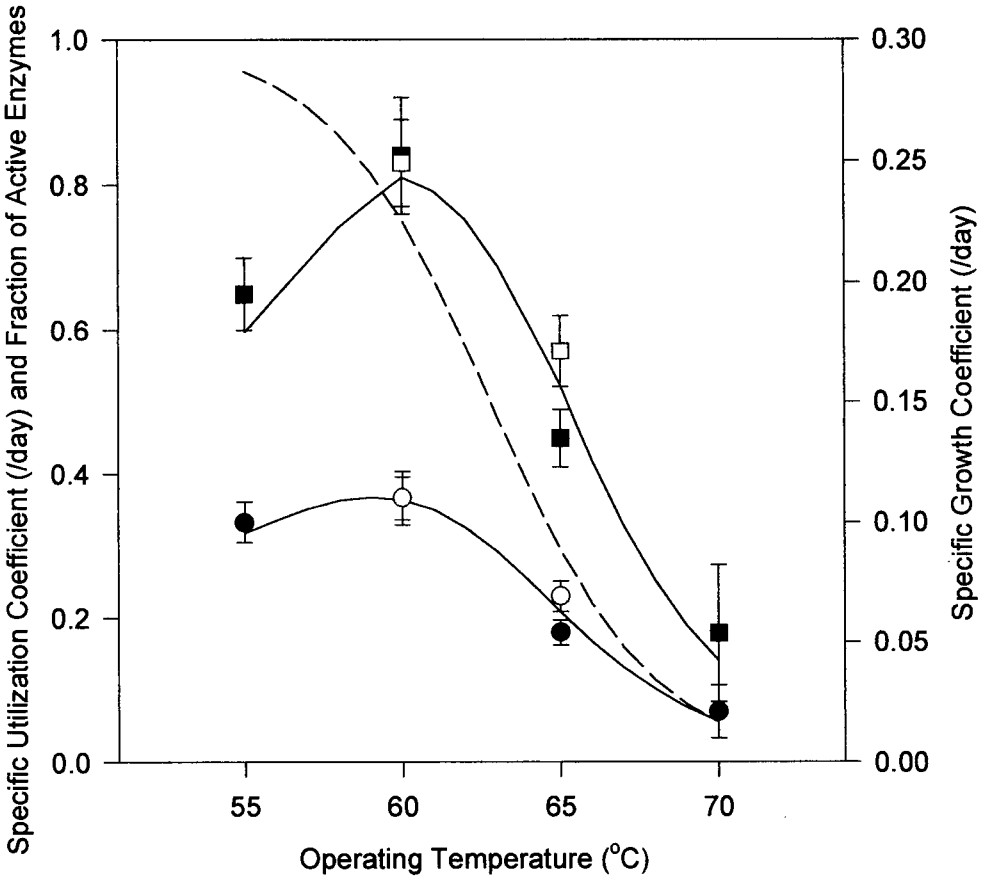


Figure 5.6 – Effect of Operating Temperature on the Specific Methanol Utilization Coefficient and the Specific Growth Coefficient

(●: specific growth coefficient; ■: specific methanol utilization coefficient; solid symbols: from Part I of study; open symbols: from Part II of study; solid lines: Equation 5.8 fitted to the estimated specific methanol utilization coefficient and the specific growth coefficient; dashed line: calculated active fraction of growth-limiting enzyme; error bars represent the 90 % confidence intervals for measurements made during the steady state monitoring periods)

Equation 5.7 has been used by others in a number of studies investigating the effects of temperature on microbial growth kinetics (Esener et al., 1981; Mayo, 1997). However, Equation 5.7 is seldom used to describe the effect of temperature on biological kinetics in wastewater treatment systems. To be applicable, an equation with a format similar to that

of Equation 5.5 would be preferable since most models used to simulate the effect of temperature on biological kinetics in wastewater treatment systems utilize that format. A new relationship, with a format similar to that of Equation 5, was proposed to describe the effect of temperature on microbial kinetics. This new relationship was derived from Equation 5.7, using the same principles as those used for deriving Equation 5.5 from Equation 5.4, as presented in Equation 5.8:

$$\mu_{T'} = \mu_D \theta^{(T'-T_D)} \left(\frac{1}{\left(1 + B' \theta'^{(T'-T_D)}\right)} \right) \qquad (5.8)$$

where θ' is the temperature inactivation coefficient for the inactivation of the biomass (-), B' is an inactivation constant (-) and the term in parentheses corresponds to the active fraction of the growth-limiting enzyme.

Equation 5.8 was fitted to the specific methanol utilization coefficients and the specific growth coefficients measured for the different operating temperatures investigated (Figure 5.6). The estimated specific methanol utilization coefficients were 0.65 ± 0.050, 0.84 ± 0.080, 0.45 ± 0.040 and 0.17 ± 0.050 /day and the specific growth coefficients were 0.10 ± 0.0084, 0.11 ± 0.011, 0.054 ± 0.0053 and 0.021 ± 0.011 /day for operating temperatures of 55, 60, 65 and 70 °C, respectively, for Part I of the present experiment. For Part II, the estimated specific methanol utilization coefficients were 0.83 ± 0.060 and 0.57 ± 0.050 /day and the specific growth coefficients were 0.11 ± 0.0080 and 0.069 ± 0.0063 /day for operating temperatures of 60 and 65 °C, respectively. Non-linear regression was used to estimate the activation and inactivation coefficients as well as the inactivation constant for Equation 5.8. As illustrated in Figure 5.6, Equation 5.8 adequately modeled the effect of temperature on the specific growth coefficient and the specific methanol utilization coefficient over the range of temperatures investigated. The estimated temperature coefficients and constants for Equation 5.8 were 1.078, 1.480 and 0.046 for θ, θ' and B', respectively, for a datum operating temperature of 55 °C. Based on these parameters, the optimal operating temperature for the removal of methanol by a mixed microbial culture was determined to be approximately 60 °C.

Equation 5.8 was also successfully fitted to data reported by others who investigated the effect of temperature on the biological uptake of substrate by microorganisms (Esener et al., 1981; Mayo, 1997). This indicates that the proposed relationship can be applied to other biological systems. However, it should be recognized that the composition of a microbial population in a mixed culture can vary significantly depending on the substrate and the operating temperature used (Sonnleitner and Fletcher, 1983). Therefore, it is reasonable to expect that different enzymes may be involved in the growth-limiting step or may predominate for different operating conditions. Consequently, the relationship presented in Equation 5 may not be valid for all wastewater treatment applications.

The effect of temperature on the growth-limiting enzyme was investigated using the term in parenthesis from Equation 5.8 with the estimated values for the activation and inactivation parameters indicated above. As illustrated in Figure 5.6, Equation 5.8 predicts a significant decrease in the fraction of active growth-limiting enzyme at temperatures of more than approximately 55 to 60 °C. This is consistent with results reported by Izumi et al. (1989). They observed that the overall activity of formate dehydrogenase, an enzyme involved in the biological oxidation of methanol to CO_2, was significantly decreased at temperatures above 55 °C. Therefore, the effect of temperature on methanol removal, as illustrated in Figure 5.6, could be due to the inactivation of formate dehydrogenase. However, further research beyond the scope of this thesis would be required to confirm this hypothesis.

As illustrated in Figure 5.6, the rate at which the operating temperature was increased significantly impacted the steady state specific methanol utilization coefficient and the specific growth coefficient above the critical operating temperature of 60 °C. This suggests that the decline in the methanol removal kinetics above the critical operating temperature of 60 °C can be more significant when the magnitude and the rate of the change in the operating temperature are larger. However, regardless of the magnitude and the rate at which the operating temperature was increased, the specific methanol utilization coefficient and the specific growth coefficient both declined significantly

when the operating temperature was increased from 60 to 65 °C as illustrated in Figure 5.6.

5.3.4 Effect of Operating Temperature on Observed Growth Yield

Off-line batch tests using radio-labeled methanol indicated that at higher temperatures, a larger fraction of the metabolized methanol were completely oxidized to CO_2 and a smaller proportion was incorporated into biomass, as illustrated in Figure 5.7. This resulted in a decrease in the observed growth yield as the operating temperature increased (Figure 5.7). Detailed results from the tests using radio-labeled methanol are presented in Table A5.60. The observed growth yields are presented in Tables A5.41 to A5.44 and Tables A5.58 to A5.59 for Parts I and II of the present experiment, respectively.

Snedecore and Cooney (1974) observed a similar decline when investigating the effect of temperature on the observed growth yield for a mixed culture of methanol-consuming microorganisms at temperatures ranging from 45 °C to 65 °C. They suggested that, at higher temperatures, microorganisms require more energy to maintain metabolic activities. Although Figure 5.7 appears to support this hypothesis, it was not possible to confirm whether the microorganisms used the additional energy produced from the more complete oxidation of methanol to CO_2 at higher temperatures. Kim et al. (1981) suggested that the decrease in the observed yield with temperature was not due to a decline in the true growth yield but to an increase in the rate of microbial decay. Muck and Grady (1974) suggested that the decrease in the observed growth yield at higher temperatures was due to a combined change in the true growth yield and an increase in the rate of microbial decay. An increase in the decay rate would likely result in an increase in the amount of non-biodegradable microbial products formed (Rittmann et al., 1987). However, as observed during Part II of the present experiment, the concentration of non-biodegradable microbial products present in the MBR at the end of selected batch feed cycles, measured as soluble TOC, was similar for the different operating temperatures investigated. For both operating temperatures of 60 and 65 °C, the residual

soluble TOC concentration in the MBR at the end of selected batch feed cycles was approximately 13 mg/L (Tables A5.45 to A5.57). This suggests that the operating temperature did not significantly affect the extent of microbial decay over the range of temperatures investigated. Further research is required to confirm the mechanisms responsible for the decline in the observed growth yield.

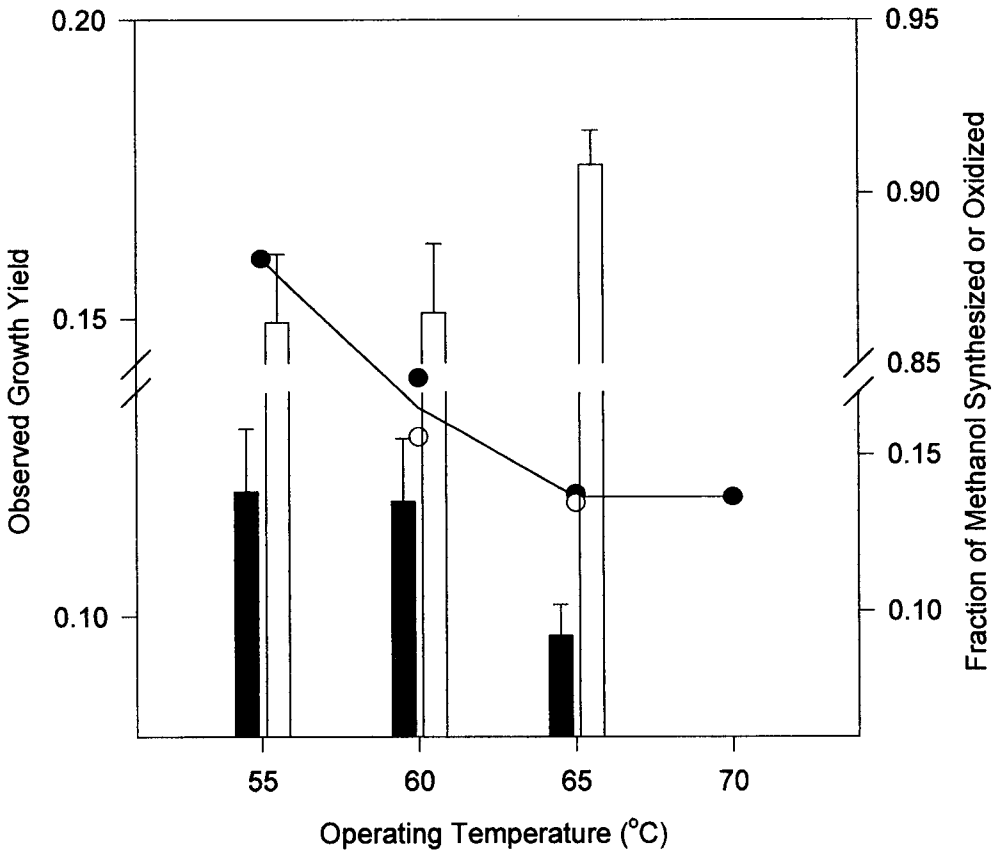


Figure 5.7 – Effect of Operating Temperature on the Observed Growth Yield and Methanol Metabolism

(•: observed growth yield; solid symbols: from Part I; open symbols: from Part II ; solid bars: fraction of methanol incorporated into biomass; open bars: fraction of methanol completely oxidized to CO_2; error bars represent the 90 % confidence intervals for measurements made during the steady state monitoring periods)

When the operating temperature was increased from 65 to 70 °C, there was no further decline in the observed growth yield. As previously mentioned, different strains of microorganisms are likely to dominate in a mixed microbial culture at different operating temperatures (Sonnleitner and Fletcher, 1983). Therefore, it is reasonable to expect that as the temperature changes, a shift in the composition of the microbial community may occur. The shift in the microbial population could explain why the observed growth yield does not continuously decrease as the temperature increases as illustrated in Figure 5.7.

The decrease in the observed growth yield at higher temperatures indicated that less excess sludge will be produced at higher temperatures. Therefore, the costs associated with waste sludge handling and disposal may be significantly lower than those for conventional biological treatment systems. In addition, the results indicate that at higher temperatures, a lower MLVSS concentration could be expected in the MBR. Although not investigated during the present study, the combined effect of lower viscosities and lower MLVSS concentrations at higher temperatures could result in a significantly higher permeate flux through the membrane component of the MBR than would be possible at lower operating temperatures (Cheryan, 1986). A higher achievable flux would reduce the costs associated with the membrane component of the MBR.

5.4 Summary

It was possible to biologically remove methanol from synthetic evaporator condensate using a high temperature MBR over the entire expected range of temperatures for evaporator condensate (55 to 70 °C). However, the operating temperature exerted a significant impact on methanol removal kinetics. A maximum specific methanol utilization coefficient and a maximum specific growth coefficient of approximately 0.84/day and 0.11 /day, respectively, were observed at an operating temperature of 60 °C. Above 60 °C, both the the specific methanol utilization coefficient and the specific growth coefficient declined sharply, suggesting that at high operating temperatures, the inactivating effect of temperature on the growth-limiting enzyme must be considered. A

relatively simple model was proposed and used to accurately estimate the effect of high temperatures on methanol removal kinetics in an MBR over the temperature range investigated. Based on the model, the optimal operating temperature for the biological removal of methanol by a mixed microbial culture was determined to be approximately 60 °C. These results indicated that it is not only possible to operate an MBR at high temperatures, but also that higher specific methanol utilization coefficients can be achieved at higher operating temperatures. However, care may need to be taken not to exceed the critical operating temperature of 60 °C.

The operating temperature also had a significant effect on the observed microbial growth yield in the MBR. At increasing operating temperatures, a larger fraction of the methanol consumed was converted to energy, reducing the observed growth yield. These results indicate that at high temperatures, less excess sludge will be produced, potentially resulting in lower waste sludge handling and disposal costs.

Chapter 6 - Effect of Contaminants Contained in Real Evaporator Condensate on the Biological Removal of Methanol

6.1 Introduction

As presented in Chapter 5, the optimal operating temperature for the biological removal of methanol from synthetic evaporator condensate was determined to be approximately 60 °C. The specific methanol utilization coefficient measured at this temperature (0.84/day) was significantly higher than that reported by others for the biological treatment of real evaporator condensate at a much lower operating temperature (Barton et al., 1996).

Real evaporator condensate contains over 60 contaminants. Table 2.1 lists compounds that are typically present in real evaporator condensate. Many of these compounds could inhibit microbial activity in a biological treatment system due to toxicological effects (Barton et al., 1996). Furthermore, the presence of non-methanolic substrates in real evaporator condensate could affect the microbial community present in a biological treatment system. As presented in Appendix 2, non-methanolic compounds, such as other alcohols, ketones and terpenes, accounted for approximately 28 % of the total organic carbon content of the evaporator condensate used during the present study. Therefore, if either of these effects occur the specific methanol utilization coefficient would be expected to decrease.

This part of the study investigated whether the relatively high specific methanol utilization coefficient observed at 60 °C (Chapter 5), using synthetic evaporator condensate, could be attributed to enhanced methanol utilization at higher operating temperatures, or to the absence of compounds that could influence methanol utilization.

6.2 Experimental Procedures and Equipment Set-Up

The effects of the evaporator condensate matrix on methanol metabolism and removal kinetics were investigated by varying the fraction of real evaporator condensate in the feed to a mixed microbial culture in an MBR from 0 % (100% synthetic evaporator condensate) to 100 % real evaporator condensate.

The investigation was subdivided into three parts. Part I determined whether the contaminants present in real evaporator condensate matrix influenced the specific methanol utilization coefficient in a high temperature MBR. Part II investigated if the contaminants present in the real evaporator condensate matrix exerted a direct toxic effect on a mixed microbial culture. Part III investigated whether the additional, non-methanolic substrates, present in a real evaporator condensate matrix, produced a change in the composition of the microbial community present in the MBR.

Part I – Identification of Effects of the Real Evaporator Condensate Matrix on Methanol Removal Kinetics

The bench scale MBR used in Part I was operated over a 20 week period from October, 1998 to February, 1999. The primary and small MBR, as described in Section 3.1, was used during Part I (primary MBR was used when feed consisted of 100 % synthetic evaporator condensate and small MBR was used when feed consisted of 10 and 100 % real evaporator condensate as presented below). The operating temperature was maintained at 60 °C (± 2 °C). Air was added at a rate of 1.6 L/minute for the primary MBR and 0.5 L/minute for the small MBR. This provided non-limiting dissolved oxygen conditions in the MBR. The primary MBR was inoculated with 2 L of activated sludge from a local kraft pulp mill and topped-off with tap water (Western Pulp Limited Partnership, Squamish, B.C.,Canada). This was repeated approximately 1 week following the initial inoculation. The feed to the MBR (primary MBR) initially consisted of a mixture of synthetic evaporator condensate and nutrients as previously presented in Chapter 5. Steady state operating conditions, based on constant rate of methanol removal

and a constant MLVSS concentration in the MBR, were reached within approximately 3 weeks following inoculation.

The effects of the evaporator condensate matrix on methanol removal kinetics were investigated by varying the fraction of real evaporator condensate in the feed to the MBR from 0 % (100% synthetic evaporator condensate) to 10% real evaporator condensate and finally to 100 % real evaporator condensate, based on the mass of methanol in the feed. The composition of the feed was based on the mass of methanol instead of the volume to maintain similar methanol loading rates for all feed compositions investigated. To keep a relatively constant methanol loading rate to the MBR, the hydraulic retention time was increased from 12 to 18 hours, when treating real evaporator condensate (i.e. the concentration of methanol in the synthetic and real evaporator condensate was approximately 500 and 900 mg/L, respectively, as presented in Appendix 2).

The mixed liquor from the primary MBR was used to inoculate the small MBR that was used when the feed contained real evaporator condensate. For each feed composition, the MBR was re-inoculated with 100 ml of activated sludge from the Western Pulp Limited Partnership bleached kraft pulp mill (Squamish, B.C.,Canada). This was done to re-introduce microorganisms that might not have been able to grow under the previous feed conditions. At each experimental setting, steady state operating conditions were reached within 1 to 2 weeks of acclimatization.

The characteristics of the synthetic evaporator condensate were as described in Section 5.2 - Part I.

The methanol removal kinetics were determined by monitoring the concentrations of methanol in the MBR over time as presented in Section 3.3. Samples were collected from the ultrafiltration cartridge effluent line and analyzed for methanol at 15, 30, 45, 60, 75, 90, 105, 120 and 175 minutes following the start of selected batch feed cycles.

Following the completion of Part I, the biomass in the MBR was inactivated, by adding sodium azide as described in Appendix A1.2, and the abiotic removal of methanol was investigated.

Part II – Identification of Direct Inhibitory Effect of Real Condensate Matrix on a Mixed Microbial Culture Acclimatized to Synthetic Evaporator Condensate

The direct toxic effects of the real evaporator condensate matrix were investigated using off-line batch treatability tests. The off-line tests were done using aliquots of mixed liquor from the MBR used during Part I when the feed consisted of 100 % synthetic evaporator condensate. The off-line, batch treatability tests were completed as described in Appendix A1.3.1.

Part III – Effect of Non-Methanolic Substances, Present in Real Evaporator Condensate Matrix, on the Microbial Community in the MBR

The effect of non-methanolic substrates, present in a real evaporator condensate matrix, on the microbial community present in the MBR was investigated using off-line batch degradation tests using radio-labeled methanol and by qualitative microbial examination. The off-line tests were done using aliquots of mixed liquor from the MBR used during Part I when the feed consisted of 0, 10 and 100 % real evaporator condensate. The off-line batch degradation tests using radio-labeled methanol were completed as described in Appendix A1.3.2. The mixed microbial culture contained in the MBR was qualitatively examined using acridine orange staining followed by observation of the microbial community using an epifluorescence microscope as described in Appendix A1.2.

6.3 Results and Discussion

This section discusses the results obtained during the third experiment investigating the effect of the contaminants present in the evaporator condensate matrix on the biological

removal of methanol from evaporator condensate. The raw data, on which this discussion is based, are presented in Appendix 6.

6.3.1 Effect of Evaporator Condensate Contaminant Matrix on Methanol Removal Kinetics

The rate of removal of methanol was observed to be constant with time and with the concentration of methanol remaining in the MBR for all feed compositions investigated as illustrated in Figure 6.1. As previously discussed (Chapters 4 and 5), the zero order removal rate for methanol, for all feed compositions investigated, indicated that the real condensate matrix did not significantly affect the half saturation and the half inhibition concentrations for methanol. This is similar to results reported by Chudoba et al. (1989) who investigated the biological oxidation of methanol in a solution containing exclusively methanol and in a solution containing methanol and non-methanolic substrates (morpholine, sulphanilic acid and nitrilotriacetic acid).

A similar first order relationship for the abiotic removal of methanol, to that observed when treating synthetic evaporator condensate (Figure 5.1), was observed when treating real evaporator condensate. As discussed in Section 5.3.2, stripping, due to the aeration system in the MBR, was responsible for the observed abiotic removal of methanol. The first order coefficient for stripping of methanol when treating real evaporator condensate was estimated to be 0.00025/minute (Table A6.20). As observed when treating synthetic evaporator condensate, stripping accounted for approximately 1 % of the mass of methanol removed from the MBR when treating real evaporator condensate.

Equation 4.4 was fitted to the concentrations of methanol in the MBR measured during selected batch feed cycles, for the different feed compositions (Figure 6.1). Linear regression was used to estimate the zero order coefficient for the biological removal of methanol for the different feed compositions examined. Results from the linear regression are presented in Tables A6.1 to A6.4, A6.5 to A6.10 and A6.11 to A6.20, for

0, 10 and 100 % real evaporator condensate in the feed, respectively. When the fraction of real evaporator condensate in the feed was increased from 0 to 10 %, there was no significant change in the zero order coefficient for the biological removal of methanol as illustrated in Figure 6.2. However, when the fraction of real evaporator condensate in the feed increased from 10 to 100 %, the zero order coefficient for the biological removal of methanol declined to a new steady state level.

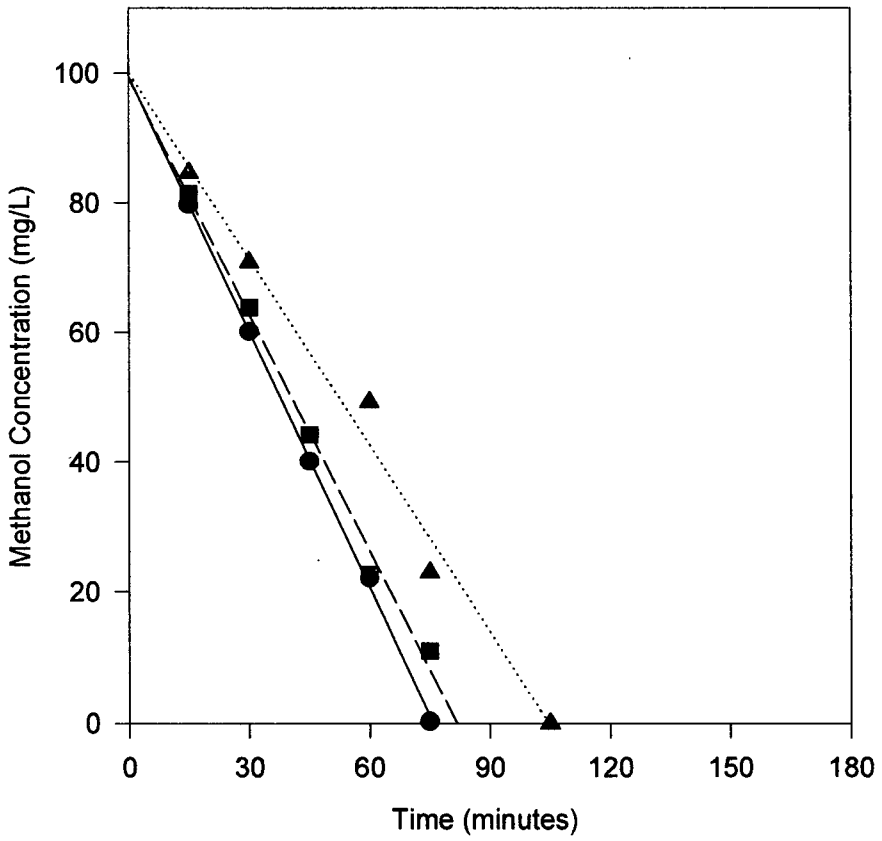


Figure 6.1 – Methanol Concentration in MBR During Typical Batch Feed Cycles for the Different Feed Compositions Investigated

(●: 0 % real condensate in feed; ■: 10 % real condensate in feed; ▲: 100 % real condensate in feed; lines: Equation 4.4 fitted to the concentration of methanol in the MBR for the different feed compositions examined)

The fraction of real evaporator condensate in the feed also significantly affected the concentration of MLVSS in the MBR as illustrated in Figure 6.3. The concentration of

MLVSS in the MBR, for the different feed conditions, are presented in Tables A6.21 to A6.23. When the fraction of real evaporator condensate in the feed was increased from 0 to 10 %, the MLVSS remained relatively constant at approximately 2100 mg/L. However, when the fraction of real evaporator condensate in the feed was increased from 10 to 100 %, the steady state concentration of MLVSS in the MBR increased to approximately 2400 mg/L. This was expected since real evaporator condensate contains a number of non-methanolic organic compounds, that can be used as substrate by a mixed microbial culture. Non-methanolic organic compounds accounted for approximately 28 % of the total organic content of evaporator condensate used during the present study, measured as TOC (Appendix 2).

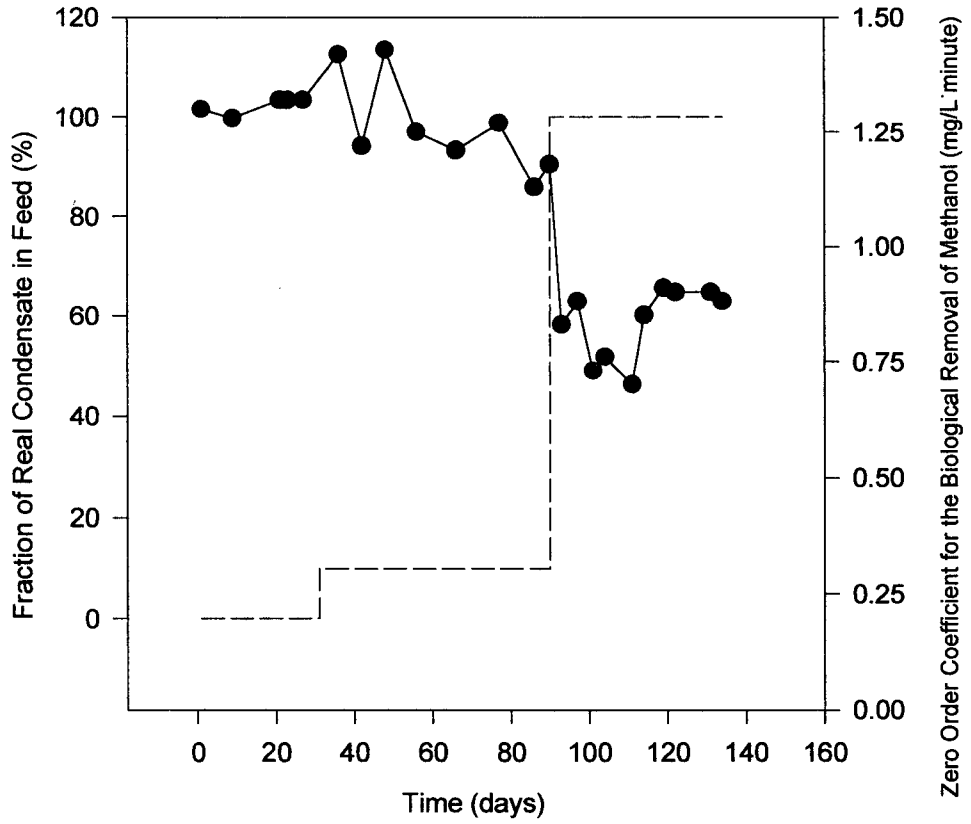


Figure 6.2 – Effect of Fraction of Real Evaporator Condensate in Feed on the Zero Order Biological Methanol Removal Coefficient

(●: zero order biological methanol removal coefficient;
dashed line: fraction of real condensate in feed)

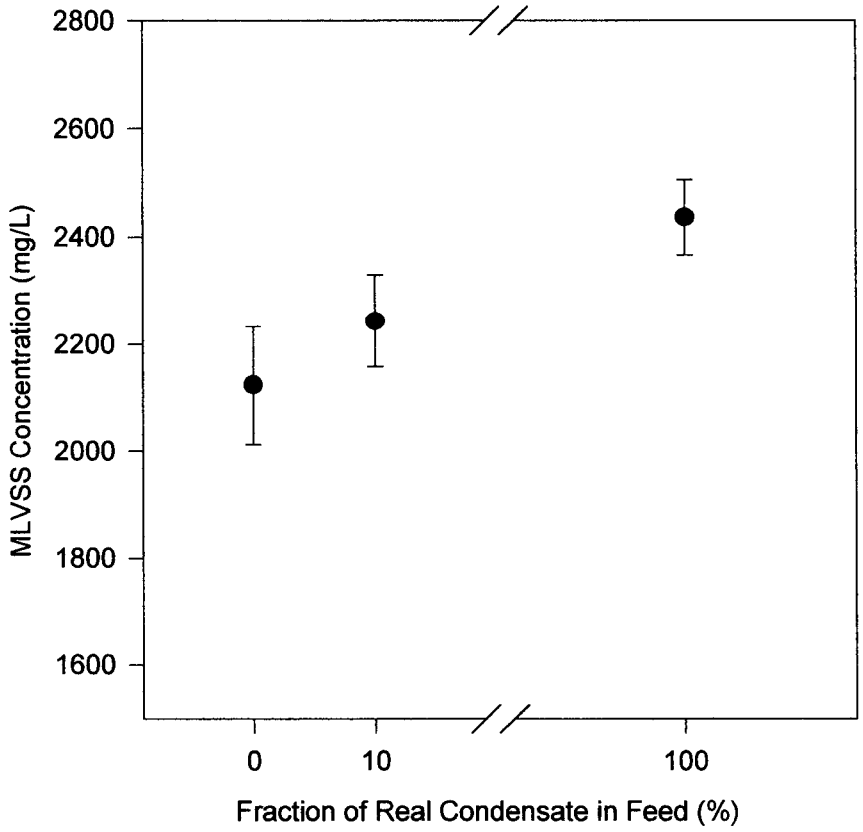


Figure 6.3 - Effect of Feed Composition on the MLVSS Concentration

(error bars represent 90 % confidence interval for measurements)

As illustrated in Figure 6.4, the combined reduction in the zero order coefficient for the biological removal of methanol and the increase in the concentration of MLVSS in the MBR when the fraction of real condensate in the feed was increased from 10 to 100 % resulted in a significant reduction in the specific methanol utilization coefficient. The specific methanol utilization coefficient decreased from approximately 0.84 ± 13 /day, when fed 0 and 10 % real evaporator condensate, to approximately 0.59 ± 011 /day, when fed 100 % real evaporator condensate. These results indicated that the evaporator condensate matrix did exert an effect on the observed specific methanol utilization coefficient in the high temperature MBR. This is similar to results reported by Chudoba et al. (1989) for the biological oxidation of methanol by a mixed microbial culture from a solution containing exclusively methanol and from a solution containing methanol and

non-methanolic substrates (morpholine, sulphanilic acid and nitrilotriacetic acid). However, they offered no explanation for their results.

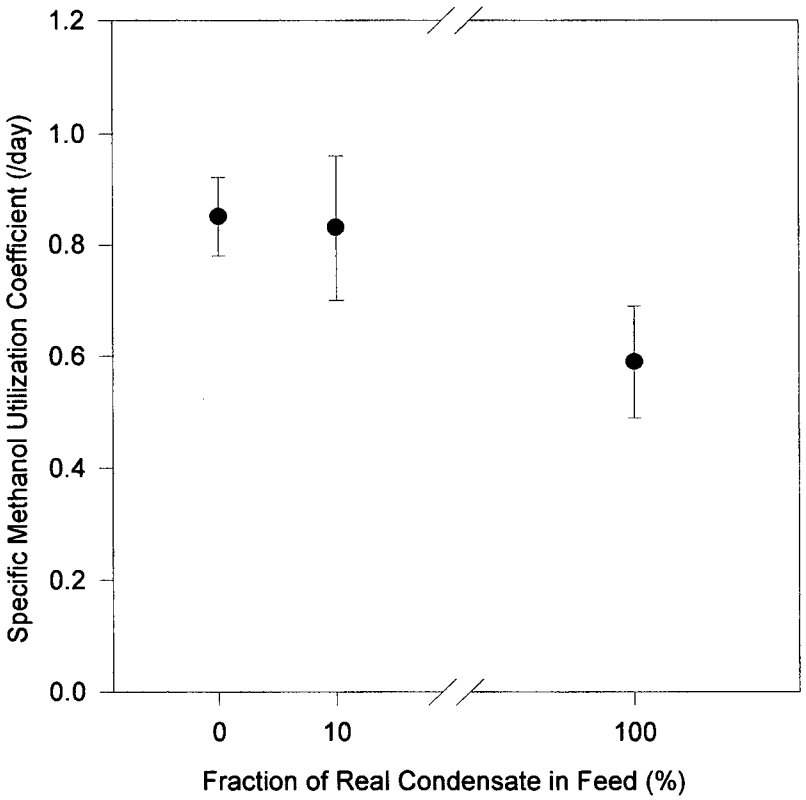


Figure 6.4 - Effect of Feed Composition on the Specific Methanol Utilization Coefficient

(error bars represent 90 % confidence interval for measurements)

6.3.2 Inhibition Due to Potentially Toxic Contaminants Contained in Real Evaporator Condensate

Off-line batch tests conducted with mixed liquor obtained from the MBR operated with synthetic evaporator condensate as feed, indicated that the potential toxic contaminants present in the real evaporator condensate matrix did not immediately affect the rate of methanol removal or the specific methanol utilization coefficient, as illustrated in Figures 6.5 and 6.6, respectively.

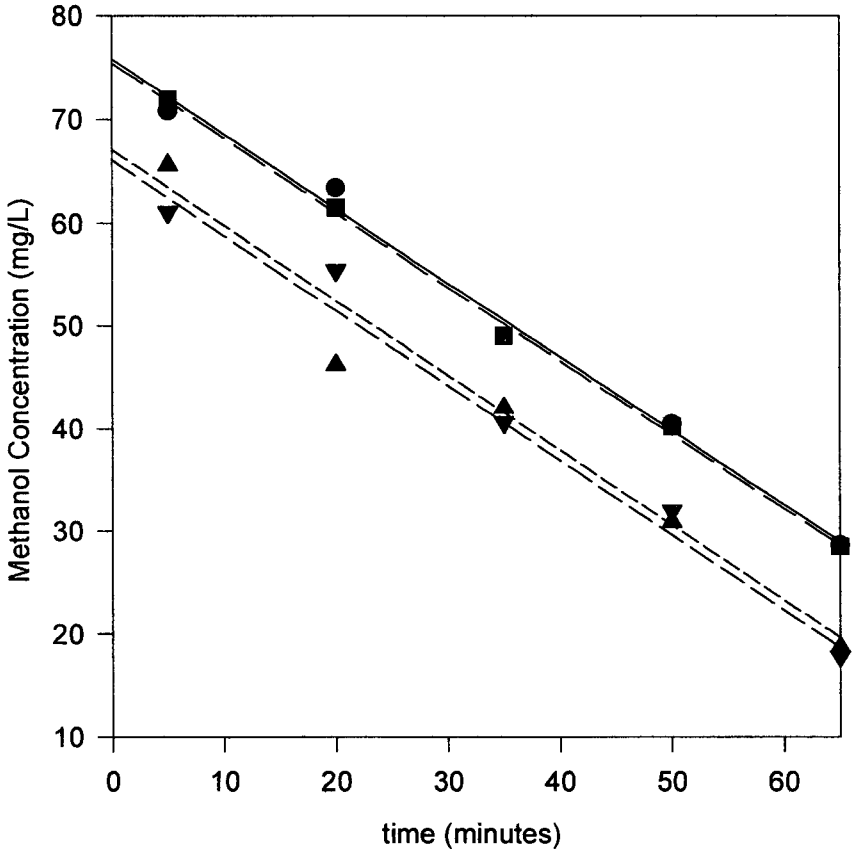


Figure 6.5 – Methanol Concentration During Typical Off-line Batch Test with Unacclimatized Biomass for the Different Feed Compositions Investigated

(● and solid line: 0 % real condensate in feed; ■ and long dashed line: 10 % real condensate in feed; ▲ and medium dashed line: 60 % real condensate in feed; ▼ and short dashed line: 100 % real condensate in feed; lines: Equation 4.4 fitted to the concentration of methanol during the off-line tests for the different feed compositions examined)

The zero order coefficients for the biological removal of methanol, from which the specific methanol utilization coefficients were calculated, were estimated by fitting Equation 4.4 to the concentrations of methanol measured during the off-line batch tests as illustrated in Figure 6.5. Linear regression was used to estimate the zero order coefficient for the biological removal of methanol. Results from the linear regression are presented

in Tables A6.24 to A6.38. Furthermore, a 10-fold increase in the suspended solids content of the real evaporator condensate, which corresponded to a suspended solids concentration of approximately 6500 mg/L, also did not produce any indication of toxicity to the unacclimatized biomass (Tables A6.35 and A6.36). From Figure 6.6, it was concluded that there were no significant direct toxic effects from the contaminants present in the real evaporator condensate matrix on the kinetics of methanol removal in an MBR.

The suspended solids concentration in the evaporator condensate used during the present study was relatively high (approximately 650 mg/L as presented in Appendix 2). The suspended solids concentration in evaporator condensate typically range from 30 to 70 mg/L (Blackwell et al., 1979). The relatively high suspended solids concentration contained in the evaporator condensate used during the present study likely originated from the physical entrainment of particulate matter during the evaporation of the black liquor.

Tests using inactivated biomass indicated that stripping of methanol during the off-line batch degradation tests did not account for a significant fraction of the methanol removed (Tables A6.37 and A6.38).

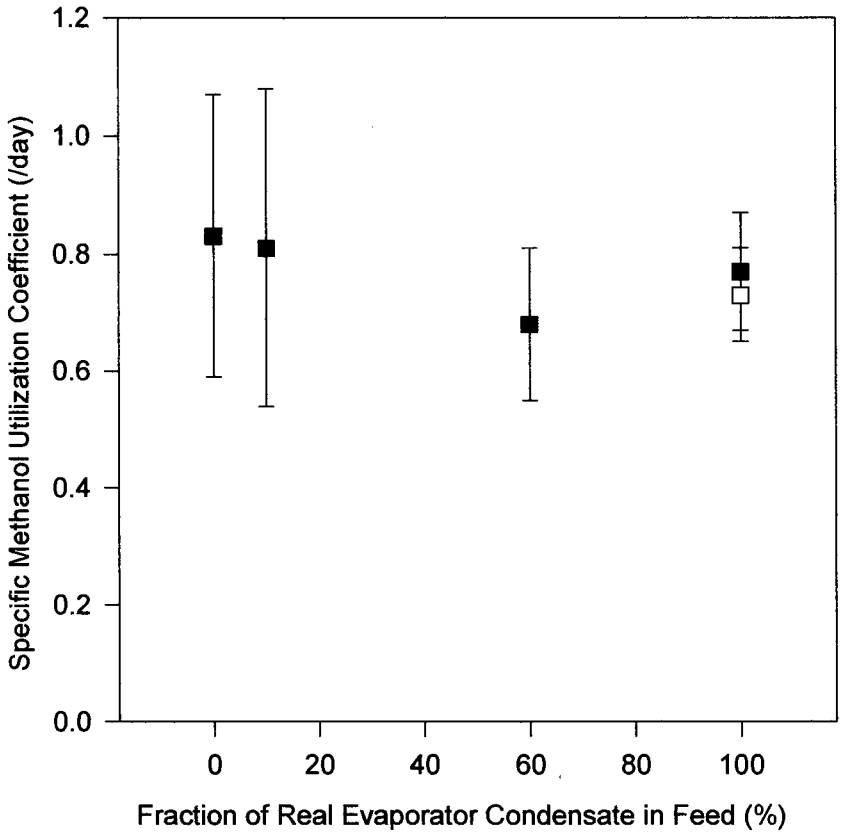


Figure 6.6 – Effect of Feed Composition on the Specific Methanol Utilization Coefficient of Unacclimated Biomass

(■: specific methanol utilization coefficient when fed evaporator condensate; □: specific methanol utilization coefficient when fed evaporator condensate with ten fold increase in suspended solids concentration; error bars represent 90 % confidence intervals)

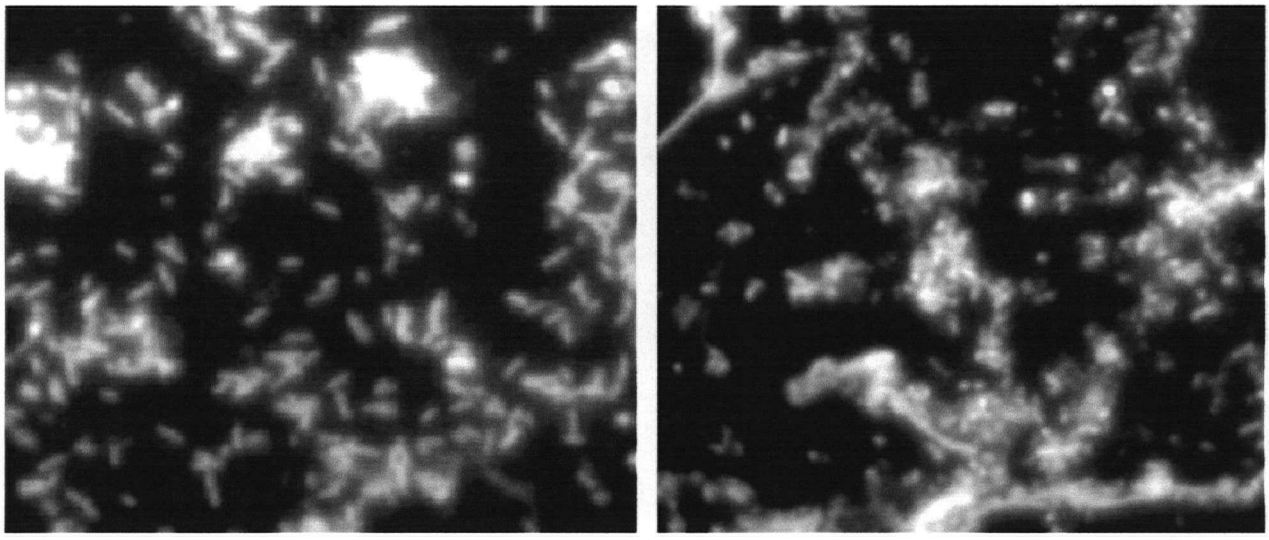
6.3.3 Effect of the Contaminants Present in Real Evaporator Condensate Matrix on the Microbial Community in the MBR

Some methanol-consuming microorganisms are capable of consuming non-methanolic substrates such as those present in real evaporator condensate (Goldberg and Rokem, 1991). However, the activity of the enzymes associated with the oxidation of methanol by these facultative methylotrophs reduced to almost non-detectable levels when non-methanolic substrates are present (O'Connor and Hanson, 1977; de Boer et al., 1990;

Izumi et al., 1989). The repression of the activity of these enzymes results in a sequential utilization of non-methanolic substrates followed by the utilization of methanol (Levering and Dijkhuizen, 1985; de Boer et al., 1990). The reduction of the enzyme activity and the sequential utilization of substrate were reported to occur almost instantaneously following the addition of non-methanolic substrates to facultative methylotrophs (Levering and Dijkhuizen, 1985; de Boer et al., 1990). An instantaneous and very low rate of methanol removal was not observed during the present study when a mixed culture of methanol consuming microorganisms was fed real evaporator condensate that contains both methanol and non-methanolic substrates (Figures 6.5 and 6.6). This suggested that the mixed culture of methanol consuming microorganisms in the MBR did not predominantly consist of facultative methylotrophs.

As presented in Picture 6.1, a qualitative examination of the mixed culture present in the MBR showed a significant difference in the morphology of microorganisms present when treating synthetic and real evaporator condensate. This indicated that the non-methanolic compounds present in real evaporator condensate had a substantial effect on the composition of the microbial community present in the MBR. When treating synthetic evaporator condensate, the microbial community appeared to consist exclusively of 0.5 μm to 1 μm, by 5 μm to 7.5 μm, rod-shaped microorganisms (Figure 6.1a). These microorganisms, hereafter referred to as methylotrophic microorganisms, were capable of growth with methanol as a sole substrate. In the real evaporator condensate feed used, approximately 28 % of the total organic carbon consisted of non-methanolic compounds. As expected, a more diversified microbial community was observed when these non-methanolic substrates were present in the feed. In addition to the previously observed rod-shaped methylotrophic microorganisms, larger rod-shaped (2 μm to 3 μm, by 10 μm to 15 μm) and filamentous microorganisms (0.5 μm to 1 μm by 50 μm to 100 μm) were noted with real evaporator condensate as feed (Picture 6.1b). These additional microorganisms were apparently only capable of growth when non-methanolic substrates, such as those contained in the real evaporator condensate matrix, were present. The qualitative examination indicated that the relative fraction of methylotrophic

microorganisms in the MBR decreased as the fraction of real evaporator condensate in the feed increased.



(a) (b)

Picture 6.1 - Qualitative Examination of Microbial Communities in MBR

((a): 100% synthetic evaporator condensate in feed; (b): 100% real evaporator condensate in feed. Note: The shutter speed for (b) was less than for (a) because the larger microorganisms in (b) were larger and therefore brighter. Consequently, the smaller rod shaped microorganisms seen in (a) are not as clearly identifiable in (b).)

As illustrated in Figure 6.7, off-line batch degradation tests using radio-labeled methanol indicated that when the feed to the MBR consisted of 100 % real evaporator condensate, a larger proportion of the methanol in the feed was oxidized to CO_2, than when the feed consisted of lower fractions of real evaporator condensate. Detailed results from the tests using radio-labeled methanol are presented in Table A6.49. These results indicated that although the "additional" microorganisms were not capable of growth with methanol as a sole substrate, at least some were capable of metabolizing methanol. Had these "additional" microorganisms not been able to consume methanol, there would not have been a change in the amount of methanol that was oxidized to CO_2. This is similar to results reported by Bitzi et al. (1991) which indicated that although some microorganisms

are not capable of growth with methanol as a sole substrate, they can use methanol as an energy source, while using non-methanolic substrates for cell synthesis. These "additional" microorganisms were defined as partial-methylotrophs since they were capable of consuming methanol, but not as sole substrate.

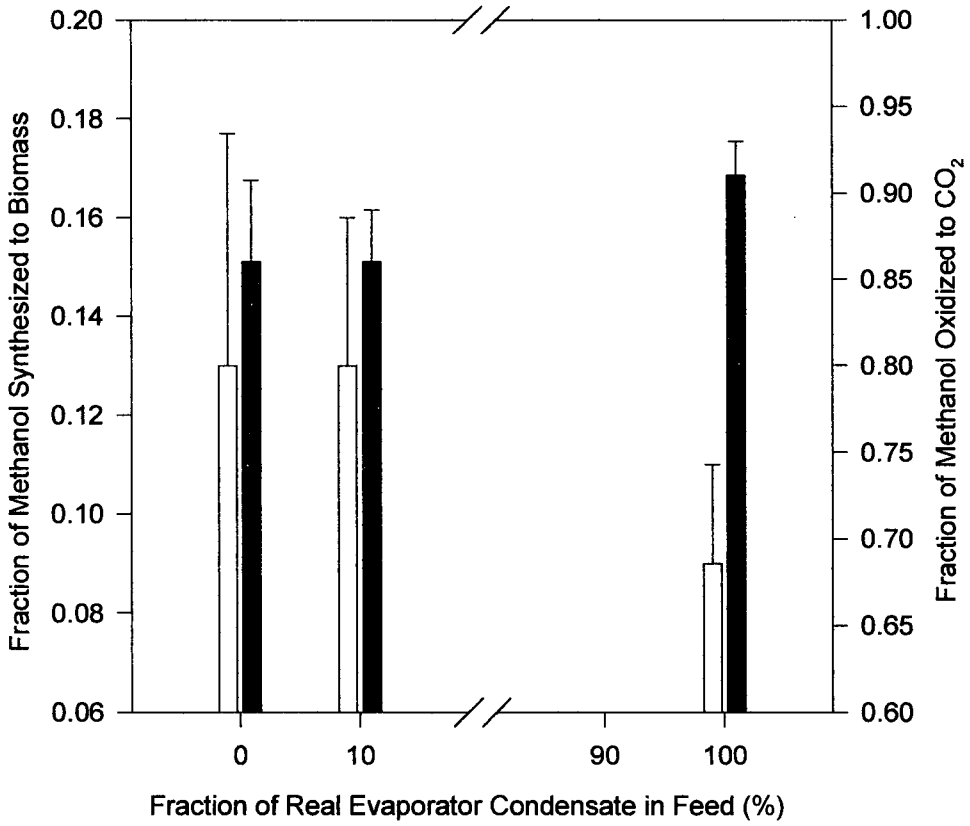


Figure 6.7 – Effect of Evaporator Condensate Matrix on Metabolism of Methanol (empty bars: fraction of methanol synthesized to biomass; solid bars: fraction of methanol oxidized to CO_2; error bars represent 90% confidence interval for measurements)

To account for the presence of two groups of microorganisms capable of metabolizing methanol when the feed to the MBR contained real evaporator condensate, Equation 4.4 was modified as presented in Equation 6.1:

$$R_{B\text{-}MeOH_f} = U_M X_{M_f} + U_{P\text{-}M} X_{N_f} \qquad (6.1)$$

where subscript M refers to methylotrophic microorganisms, subscript P-M refers to partial-methylotrophic microorganisms and subscript f refers to the fraction of real evaporator condensate in the feed.

At steady state, the concentrations of methylotrophic microorganisms for each feed composition examined can be estimated from the ratio of its observed growth yield to the total observed growth as presented in Equation 6.2:

$$X_{M_f} = \left(\frac{Y_{M_f}}{Y_{To_f}} X_{To_f} \right) \qquad (6.2)$$

where subscript To refers to the total for both methylotrophic and non-methylotrophic microorganisms; the total observed growth yield for each feed composition examined are presented in Tables A6.21 to A6.23.

The observed growth yield for methylotrophic microorganisms for each feed composition examined was estimated based on the results from the off-line degradability tests using radio-labeled methanol as presented in Equation 6.3:

$$Y_{M_f} = Y_{To_{(f=0\%)}} \left(\frac{\text{Methanol Synthesized to Biomass}_f}{\text{Methanol Synthesized to Biomass}_{(f = 0\%)}} \right) \qquad (6.3)$$

where Methanol Synthesized to Biomass refers to the fraction of radio-labeled methanol which is synthesized to biomass (Figure 6.7).

The concentrations of partial-methylotrophic microorganisms for each feed composition examined were estimated to be the difference between the total MLVSS concentration and the MLVSS concentration of methylotrophic microorganisms.

Based on Equations 6.2 and 6.3, the concentrations of methylotrophic microorganisms and partial-methylotrophic microorganisms were estimated and are illustrated in Figure 6.8. The lines presented in Figure 6.8 are to illustrate a general trend and are not meant to imply any direct relationship between the MLVSS concentration and the fraction of real evaporator condensate in the feed. Additional tests would be required to establish a relationship.

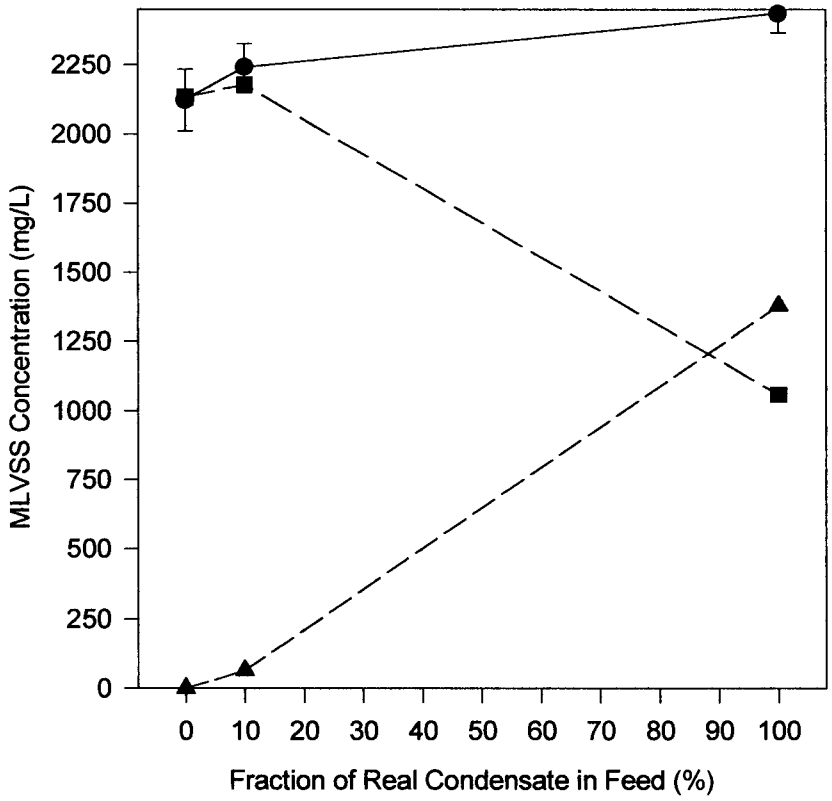


Figure 6.8 – Estimated Concentration of Methylotrophic and Partial-Methylotrophic Microorganisms in the MBR for Different Feed Compositions

(● and solid line: measured total MLVSS; ■ and long dashed line: estimated concentration of methylotrophic microorganisms; ▲ and short dashed line: estimated concentration of partial-methylotrophic microorganisms)

From Equation 6.1 and the estimated concentrations of each group of methanol-utilizing microorganisms for each real condensate fraction in the feed examined, the specific

methanol utilization coefficient for partial-methylotrophic microorganisms (U_{P-M}) was estimated to be approximately 0.29/day when treating real evaporator condensate at 60 °C. This value is substantially lower than the specific methanol utilization coefficient measured for methylotrophic microorganisms only. The specific methanol utilization coefficient for methylotrophic microorganisms (U_M) was assumed to be equal to the specific methanol utilization coefficient measured when 100 % synthetic evaporator condensate was used as feed (0.84/day).

These results indicated that as the fraction of real evaporator condensate in the feed was increased, more of the methanol was consumed by partial-methylotrophic microorganisms, leaving less methanol available for the methylotrophic microorganisms. This reduced the concentration of methylotrophic microorganisms present in the MBR mixed liquor. Similar results were reported by Al-Awadhi et al. (1990) who investigated a binary culture containing methylotrophic and partial-methylotrophic bacteria. They observed that when the binary culture was fed methanol and non-methanolic (ethanol) substrates, the number of methylotrophic bacteria, measured by direct microbial count, decreased. The competition for the available methanol observed in the present experiment, resulted in a reduction in the overall specific methanol utilization coefficient as the methylotrophic microorganisms, which consume methanol at a faster rate, were replaced by partial-methylotrophic microorganisms, which consume methanol at a slower rate.

6.3.4 Discussion

The overall specific methanol utilization coefficient measured in the present experiment when treating 100 % real evaporator condensate was 0.59 ± 0.11/day. This is more than 30 % higher than previously reported by others for a biological system treating evaporator condensate at much lower temperatures. Barton et al. (1996) reported a specific methanol utilization coefficient of approximately 0.45/day in a batch activated sludge system treating combined evaporator condensate at 33 °C. However, as observed

in the present experiment, the composition of the evaporator condensate matrix can significantly affect the methanol removal kinetics. Therefore, it is not possible to confirm whether the lower observed specific methanol utilization coefficient reported at lower operating temperatures is due to the effect of the operating temperature, or to matrix effects associated with evaporator condensate that may have different characteristics. Nonetheless, the present study confirms that it is possible to achieve high methanol removal rates from evaporator condensate using a high temperature biological treatment system such as an MBR.

As previously discussed, the removal of methanol is one of the primary objectives of evaporator condensate treatment for reuse. As observed in the present experiment, the rate of removal of methanol decreased when other non-methanolic substrates were present in the biological treatment system. Therefore, the evaporator condensate should be treated separately from other waste streams. Combining the evaporator condensate with other waste streams, such as the bleach plant filtrates or whitewater, before treatment would likely reduce the overall removal rate for methanol.

6.4 Summary

The specific methanol utilization coefficient measured during the treatment of real evaporator condensate was lower than that previously observed with synthetic evaporator condensate. The difference was not due to a direct toxic effect from compounds present in the real evaporator condensate matrix. The reduction was attributed to a shift in the composition of the microbial community present in the MBR. The shift resulted from competition between partial-methylotrophic and methylotrophic microorganisms for the available methanol. The partial-methylotrophic microorganisms exhibited a lower specific methanol utilization coefficient (0.29/day) than the methylotrophic microorganisms (0.84/day), resulting in a lower overall specific methanol utilization coefficient of 0.59 ± 0.11 /day. Nonetheless, the specific methanol utilization coefficient observed in the present experiment, at 60 °C, was still more than 20 % higher than

previously reported values from other studies of biological treatment of evaporator condensate at much lower temperatures.

Chapter 7 – Removal of Non-Methanolic Contaminants from Evaporator Condensate During High Temperature Biological Treatment

7.1 Introduction

As discussed in Section 2.2, methanol was identified as the primary contaminant of concern contained in evaporator condensate. The removal of methanol from evaporator condensate was investigated in experiments 1 through 3 as presented in Chapters 4 to 6. However, as outlined in Section 2.2, evaporator condensate also contains a number of secondary contaminants of concern that must also be removed before the evaporator condensate can be reused as process water. Of particular concern are the trace organic compounds, such as non-methanolic alcohols, ketones, terpenes, phenolics, acids and aldehydes, as well as hydrogen sulphide and methyl mercaptan contained in the evaporator condensate. Organic compounds can disrupt the pulping process and cause biological growth in mill process piping and equipment, as discussed in Sections 2.2.2 and 2.2.3. Hydrogen sulphide and methyl mercaptan can produce unpleasant or even hazardous working conditions for mill staff, as discussed in Section 2.2.1.

This part of the study investigated the removal of non-methanolic contaminants of concern from evaporator condensate during high temperature biological treatment. Knowledge of the removal kinetics and fate of these secondary contaminants of concern during treatment is necessary to properly evaluate the applicability of high temperature biological treatment, using an MBR, for the treatment of evaporator condensate for reuse.

It is difficult to monitor the removal of each non-methanolic contaminant individually because of the large number of organic compounds contained in the evaporator condensate and because most are present at trace levels. Instead, total organic carbon (TOC) was selected as a multi-component parameter to measure the concentration of all organic compounds present in evaporator condensate. TOC was selected over other commonly used multi-component measurements such as biological oxygen demand

(BOD) and chemical oxygen demand (COD) mainly because the procedure for TOC analysis is fast, relatively simple and the results are highly reproducible.

7.2 Experimental Procedures and Equipment Set-up

The removal of non-methanolic contaminants of concern from the evaporator condensate was monitored during Part I of the experimental program outlined in Chapter 6, using 100 % real condensate in the feed.

The removal of non-methanolic organic material was monitored by measuring the change in the concentration of TOC and methanol in the MBR during selected batch feed cycles as presented in Section 3.3. The concentration of methanol, expressed as a TOC equivalent, was calculated by multiplying the methanol concentrations by a ratio of 12/32 (ratio of the weight of carbon in methanol to the weight of methanol in one mole). The abiotic TOC removal was monitored when the biomass in the MBR was inactivated using sodium azide as presented in Section 6.2.

A mass balance calculation was also performed around the MBR to determine the fate of the RSC contained in the evaporator condensate during high temperature biological treatment using an MBR. The experimental procedure and set-up for the mass balance are presented in Appendix A1.4.

7.3 Removal of Non-Methanolic Organic Contaminants

This section discusses the results obtained when investigating the removal of non-methanolic organic contaminants from evaporator condensate using a high temperature MBR. The raw data, on which this discussion is based, are presented in Appendix 6.

7.3.1 Degradable and Non-Degradable Components of Multi-Component Substrate

As illustrated in Figure 7.1, the concentration of TOC in the MBR was reduced from approximately 90 mg/L to approximately 50 mg/L during each batch feed cycle. After approximately 100 minutes following the start of the batch feed cycle, there was no longer any significant reduction in the concentration of TOC although a relatively high residual concentration of TOC remained in the MBR.

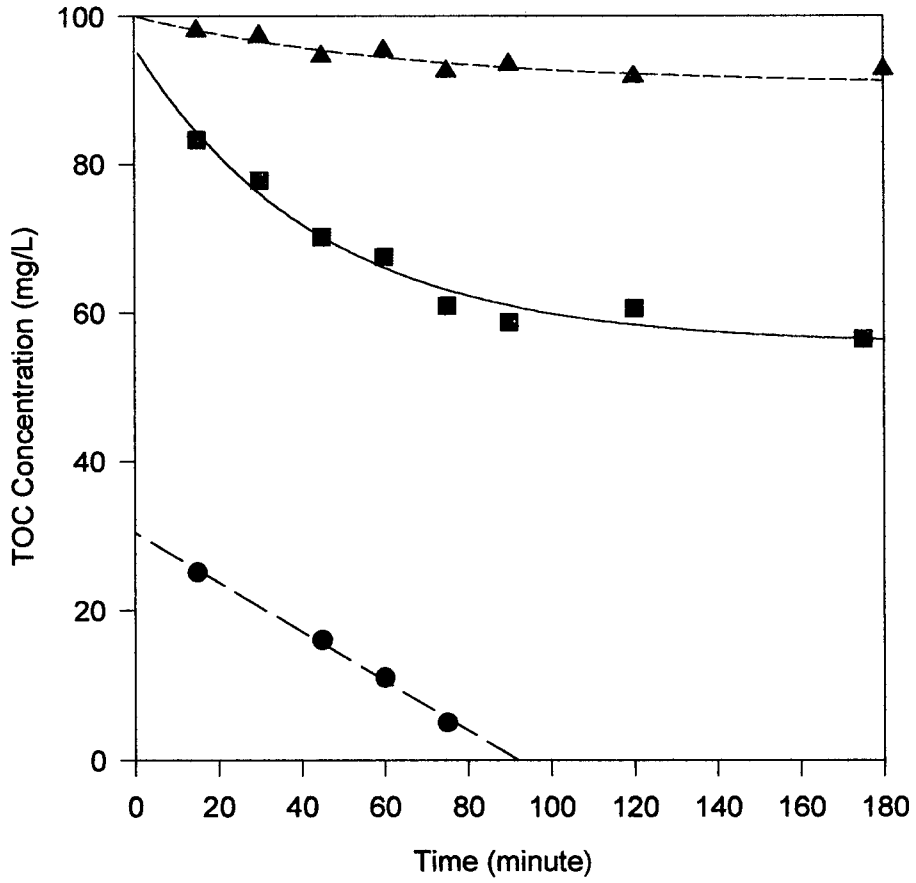


Figure 7.1 – TOC Concentration in MBR During a Typical Batch Feed Cycle
(●: methanol (expressed as TOC); ■: total TOC; ▲: TOC removal with inactivated biomass; solid line: Equation 7.6 fitted to the TOC concentration; long dashed line: Equation 4.4 fitted to the concentration of methanol as TOC; small dashed line: Equation 7.1 fitted to the TOC concentrations measured during tests with inactivated biomass)

When the biomass was inactivated, the reduction in TOC occurred at a much slower rate as illustrated in Figure 7.1. The abiotic TOC removal rate followed a first order relationship similar to the one presented in Equation 4.2, for the stripping of volatile compounds from the MBR due to the aeration system. A first order relationship, for the stripping of the volatile component of the TOC contained in the evaporator condensate due to the aeration system, was developed as presented in Equation 7.1:

$$\frac{dS}{dt} = K_{STRIP\text{-}TOC}(S - S_{NS}) \qquad (7.1)$$

where S is the concentration of the multi-component substrate (mg/L as TOC), S_{NS} is the non-volatile component of the multi-component substrate, and $K_{STRIP\text{-}TOC}$ is the first order coefficient for stripping of TOC (/minute).

Equation 7.1 was fitted to the concentrations of TOC in the MBR measured during the abiotic tests. Non-linear regression was used to estimate the first order coefficient for stripping of TOC. Results from the linear regression are presented in Tables A6.20. The first order coefficient for stripping of TOC was estimated to be 0.014 /minute. At this rate, stripping accounted for less than 5 % of the mass of TOC removed from the MBR. The TOC removal measured during the test using inactivated biomass is presented in Figure 7.1.

A number of semi-empirical relationships have been developed to model the biological removal of a multi-component substrate by a mixed culture of microorganisms (Tisher and Eckenfelder, 1968; Grady and Williams, 1975; Grau et al.,1975; Elmaleh and Ben Aim, 1976). These relationships assume that the removal rate of a multi-component substrate is a function of the number of components remaining, and that the number of components remaining can be estimated by the concentration of multi-component substrate remaining (Grau et al., 1975).

Tisher and Eckenfelder (1968) proposed that the sum of the removal rates for the individual components of the multi-component substrate, could be approximated by a first order relationship as presented in Equation 7.2:

$$\frac{dS}{dt} = U_{TOC\text{-}72} X S \qquad (7.2)$$

where $U_{TOC\text{-}72}$ is the first order specific TOC utilization coefficient for Equation 7.2 (mg/L·day).

Grady and Williams (1975) observed that the removal rate for a multi-component substrate was not only a function of the concentration of the multi-component substrate remaining, but also a function of the initial substrate concentration. They proposed that the removal rate for a multi-component substrate could be modeled as presented in Equation 7.3:

$$\frac{dS}{dt} = U_{TOC\text{-}73} X \frac{S}{S_O} \qquad (7.3)$$

where S_O is the initial concentration of the multi-component substrate (mg/L) and $U_{TOC\text{-}73}$ is the first order specific TOC utilization coefficient for Equation 7.3 (/day).

Adams et al. (1975) compared the relationships presented in Equations 7.2 and 7.3. They observed that the relationship presented in Equation 7.3 more accurately modeled the removal rate during the biological treatment of wastewater, especially when the composition of the wastewater varied. Considering that the characteristics of the evaporator condensate are relatively variable, as presented in Appendix 2, the relationship presented by Grady and Williams (1975) for TOC removal from evaporator condensate during high temperature biological treatment may be a suitable choice to model TOC removal in an MBR.

Elmaleh and Ben Aim (1976) proposed that the removal of a multi-component substrate by a mixed culture of microorganisms could be approximated by a Monod-type relationship as presented in Equation 7.4:

$$\frac{dS}{dt} = U_{TOC\text{-}74} X \left(\frac{S}{S + aS_O} \right) \qquad (7.4)$$

where $U_{TOC\text{-}74}$ is the pseudo-first order specific TOC utilization coefficient for Equation 7.4 (/day) and a is a constant (-).

They remarked that the relationship presented by Grady and Williams (1975) was a special case for which S is small in comparison to aS_O.

The semi-empirical relationships proposed by Tisher and Eckenfleder (1968), Grady and Williams (1975) and Elmaleh and Ben Aim (1976) assume that the removal rate for a multi-component substrate is proportional to the multi-component substrate concentration remaining. However, this assumption is incorrect when the concentration of the individual components is not proportional to their respective degradabilities (Grau et al., 1975; Orhon et al. ,1990). To account for a potential non-linear relationship between the concentrations of the individual components and their degradabilities, Grau et al. (1975) proposed that the removal rate for a multi-component substrate could be estimated as an n^{th} order relationship as presented in Equation 7.5:

$$\frac{dS}{dt} = U_{TOC\text{-}75} X \left(\frac{S}{S_O} \right)^n \qquad (7.5)$$

where n is a constant not limited to integers and $U_{TOC\text{-}75}$ is the n^{th} order specific TOC utilization coefficient for Equation 7.5 (/day).

For most applications of multiple-component substrate removal, the exponent n in Equation 7.5 is either 1 or 2 (Grau et al., 1975). For n=1, the relationship suggested by

Grau et al. (1975) is similar to the relationship proposed by Grady and Williams (1975). Adams et al. (1975) remarked that for most biological treatment systems, the removal rate for a multi-component substrate follows a first order removal relationship where n=1.

These semi-empirical relationships presented in Equations 7.2 to 7.5 were fitted to the concentration of TOC in the MBR measured during selected batch feed cycles as illustrated in Figure 7.2. Non-linear regression was used to estimate the specific TOC utilization coefficients presented in Equations 7.2 to 7.5. These relationships did not accurately model the removal of TOC from the evaporator condensate during biological treatment (Figure 7.2). The relationships presented in Equations 7.2 to 7.4 and Equation 7.5 for n = 1, produced identical results when fitted to the concentration of TOC in the MBR (solid line in Figure 7.2). These relationships substantially underestimated the removal of TOC during the initial part of the batch feed cycle and substantially overestimated the removal of TOC during the remainder of the batch feed cycle as illustrated in Figure 7.2. The relationships presented in Equation 7.5 for n = 2, fitted the concentration of TOC in the MBR slightly better (long dashed line in Figure 7.2). However, this relationship also substantially underestimated the removal of TOC during the initial part of the batch feed cycle and substantially overestimated the removal of TOC during the remainder of the batch feed cycle as illustrated in Figure 7.2. The relationship that best fitted the concentration of TOC in the MBR was Equation 7.5 for n = 6.89 (medium dashed line in Figure 7.2). However, this relationship substantially overestimated the removal of TOC during the initial part of the batch feed cycle and substantially underestimated the removal of TOC during the middle part of the batch feed cycle as illustrated in Figure 7.2. The poor agreement of these semi-empirical relationships with the measured concentrations of TOC in the MBR was attributed to an assumption made during the development of the above relationships. The relationships presented in Equations 7.2 to 7.5 assume that the removal rate for the multi-component substrate is a function of the concentration of the multi-component substrate remaining in the system. When a significantly large fraction of the multi-component substrate is non-biodegradable, as observed during the present experiment, there may be no relationship

between the removal rate and the concentration of the multi-component substrate remaining.

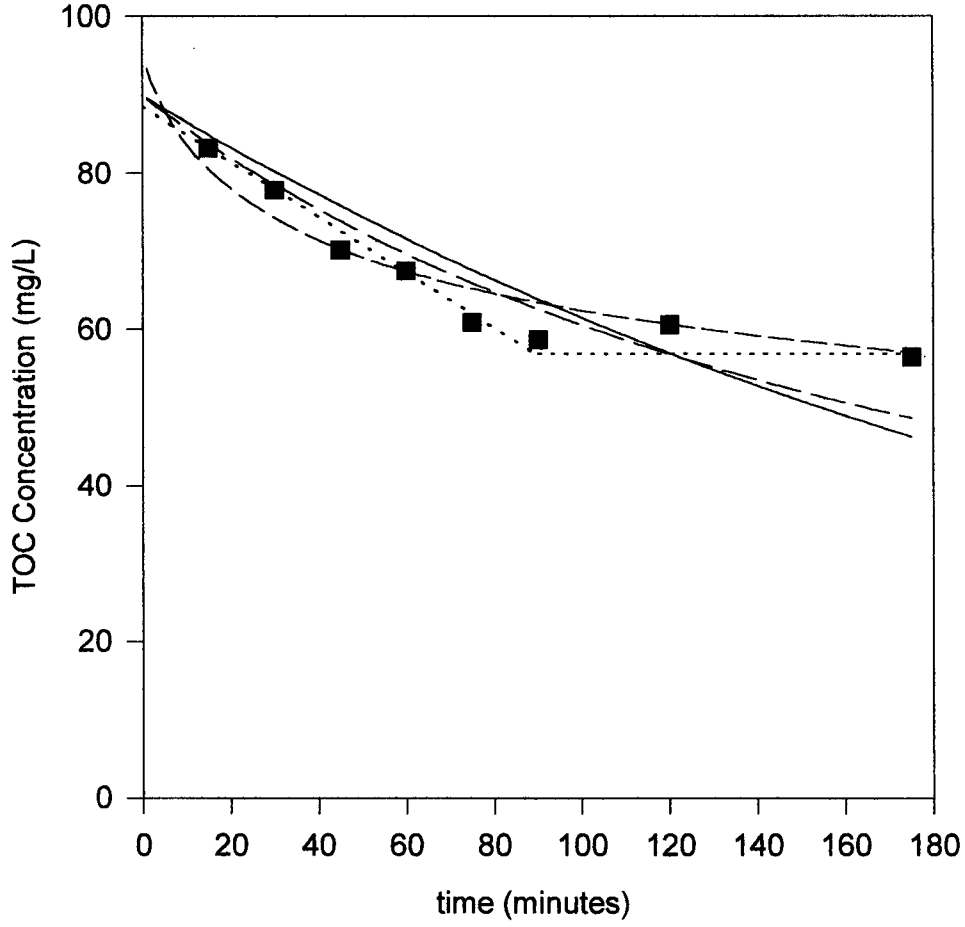


Figure 7.2 – Relationships Presented in Equations 7.2 to 7.5 Fitted to TOC Concentrations in MBR Measured During a Typical Batch Feed Cycle

(■: total TOC; solid line: Equations 7.2 to 7.4 and Equation 7.5 for n = 1, fitted to the TOC concentration; long dashed line: Equation 7.5 for n = 2, fitted to the TOC concentration; medium dashed line: Equation 7.5 for n = 6.89, fitted to the TOC concentration; short dashed line: two sequential zero order relationships fitted to TOC concentration)

To account for the presence of non-biodegradable compounds in evaporator condensate, the multi-component substrate was divided into a biodegradable component and a non-biodegradable component. Substituting the biodegradable and non-biodegradable components into Equation 7.5 for n = 1 yields Equation 7.6:

$$\frac{dS}{dt} = U_{TOC-76} X \left(\frac{S - S_N}{S_O - S_N} \right) \qquad (7.6)$$

where S_N is the non-biodegradable component of the multi-component substrate (mg/L) and U_{TOC-76} is the first order specific utilization coefficient for Equation 7.6 (/day).

Equation 7.6 was successfully fitted to the TOC concentrations in the MBR, measured during selected batch feed cycles, as illustrated in Figure 7.1. Therefore, when dealing with waste streams that contain a relatively large non-biodegradable component, such as evaporator condensate, the semi-empirical relationships developed to model the uptake of a multi-component substrate by a mixed culture of microorganisms, presented in Equation 7.2 to 7.5, must be modified to account for the non-biodegradable component. Non-linear regression was used to estimate the non-biodegradable component of the influent TOC and the first order specific TOC utilization coefficient (hereafter referred to as the specific TOC utilization coefficient). Results from the non-linear regression are presented in Tables A6.11 to A6.19. The MLVSS concentrations used to estimate the specific TOC utilization coefficient are presented in Table A6.23. The specific TOC utilization coefficient was estimated to be 0.66 ± 0.056 /day. The concentration of non-biodegradable component of the multi-component substrate in the MBR when treating evaporator condensate was estimated to be 52 ± 3.6 mg/L (as TOC).

Equation 7.6 suggests that the TOC removal rate declined over time. As illustrated in Figure 7.1, the initial TOC removal rate at the start of a batch feed cycle was higher than that for methanol (as TOC). Therefore, at the start of a batch feed cycle, some non-methanolic organic compounds were likely rapidly removed from the liquid phase in the MBR. Considering that stripping did not account for a significant fraction of the TOC

removed, the initial rapid reduction in the concentration of TOC in the MBR was likely due to the biological removal of compounds, such as ethanol and acetone, which have been reported to be more rapidly consumed than methanol (Pitter and Chudoba, 1990; Al-Awadhi et al., 1990; Bitzi et al., 1991).

The residual TOC concentration in the MBR at the end of each feed cycle did not vary significantly, even though the influent TOC concentration varied significantly. The 90 % confidence interval for the TOC concentration remaining in the MBR at the end of selected batch feed cycles was ± 3.6 mg/L. The 90 % confidence interval for the TOC concentration in the influent evaporator condensate was ± 137 mg/L. This indicated that the non-biodegradable component of the TOC in evaporator condensate does not vary considerably and that a relatively constant effluent TOC concentration can be expected following treatment with a high temperature MBR even with fluctuating influent TOC concentrations.

As presented in Figure 7.2, the TOC concentration in the MBR could also be modeled using two sequential zero order relationships similar to that presented in Equation 4.4 for the removal of methanol. However, the overall removal of TOC from the MBR was more accurately modeled using the relationship presented in Equation 7.6, than using two sequential zero order relationship (the coefficient of determination associated with two sequential zero order relationships (0.717 ± 0.109) was significantly lower than that associated with the relationship presented in Equation 7.6 (0.955 ± 0.04) when fitted to the observed TOC concentrations in the MBR as presented in Tables A6.11 to A619 in Appendix 6). This was expected since for the removal of a multi-component substrate to follow a zero order relationship, the individual components of the substrate would all have to be removed following a zero order relationship and be fully exhausted from the mixed liquor all at the exact same time (Grau et al., 1975; Chudoba, 1990).

7.3.2 Formation of Non-Degradable Microbial Products

Chudoba (1985) suggested that non-biodegradable organic compounds contained in the effluent from a biological treatment system consist of non-biodegradable compounds originally present in the untreated wastewater and soluble non-biodegradable compounds produced by the mixed culture of microorganisms during treatment. Chudoba (1985) observed that the amount of non-biodegradable microbial products produced by a mixed culture was proportional to the initial amount of biodegradable substrate present in the wastewater. Rittmann et al. (1987) observed that in addition to the initial amount of biodegradable substrate present in the wastewater, the amount of non-biodegradable microbial products produced by a mixed culture was also proportional to the concentration of active biomass in the system.

The formation of microbial products was investigated for the treatment of synthetic evaporator condensate by monitoring the concentration of methanol, expressed as TOC, and the concentration of soluble TOC in the MBR during selected batch feed cycles (Figure 7.3). The synthetic evaporator condensate contained methanol as sole substrate. The difference in the concentration of soluble TOC and methanol (expressed as TOC) was assumed to correspond to the amount of soluble microbial products present in the MBR. As illustrated in Figure 7.3, the concentrations of soluble TOC in the MBR during selected batch feed cycles were higher than the concentrations for methanol (expressed as TOC) indicating that soluble microbial products were formed in the MBR. When methanol was completely removed from the MBR, there was no further significant change in the concentration of soluble TOC in the MBR as illustrated in Figure 7.3. This suggested that the soluble microbial products were not biodegradable. The relatively constant soluble TOC concentration in the MBR following the complete removal of methanol also suggested that during high temperature biological treatment, the majority of the non-biodegradable microbial products were formed mainly as a result of substrate metabolism rather than from cell lysis as suggested by Rittmann et al. (1987). Had cell lysis been a significant contributor to the formation of non-biodegradable microbial

products, the concentration of TOC in the MBR would have been expected to increase once all of the methanol had been completely removed from the MBR.

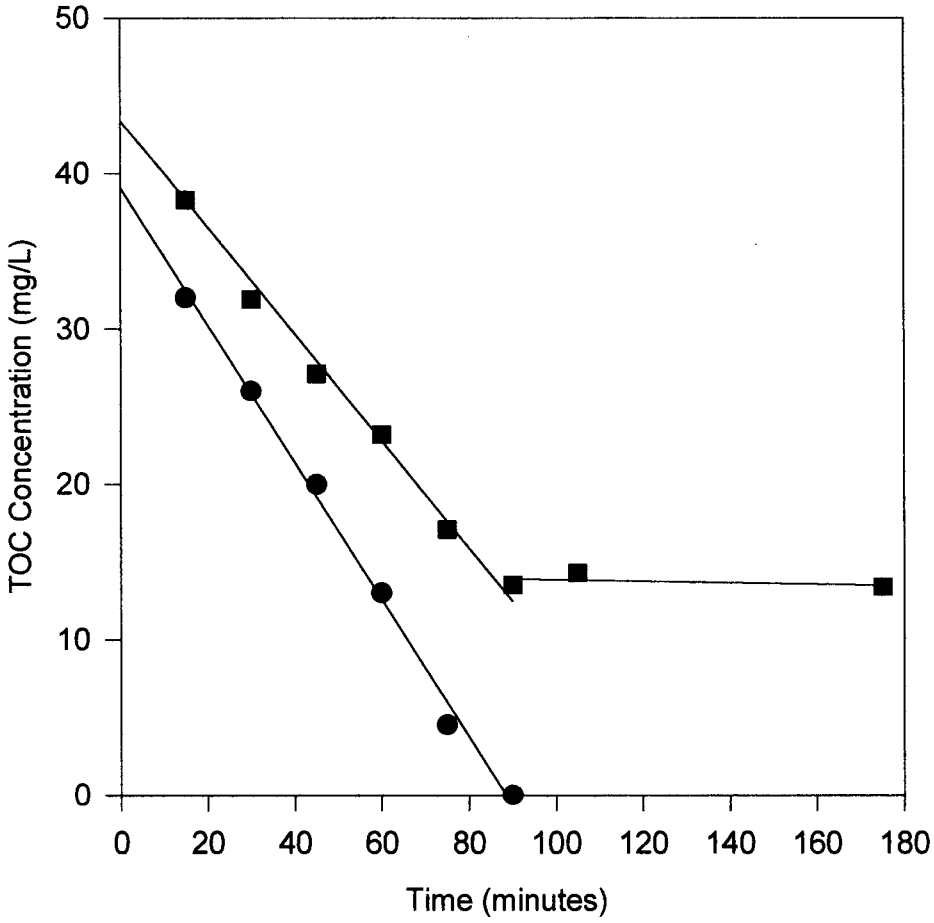


Figure 7.3 – TOC Concentration in MBR with Synthetic Evaporator Condensate as Feed During a Typical Batch Feed Cycle

(●: methanol (expressed as TOC); ■: TOC)

The residual concentration of non-biodegradable microbial products (soluble TOC) in the MBR at the end of a batch feed cycle was relatively constant throughout the present study. This indicated that the non-biodegradable microbial products were not retained by the membrane component of the MBR. Had these non-biodegradable microbial products not been able to permeate through the membrane, the residual concentration of non-

biodegradable microbial products in the MBR at the end of a batch feed cycle would have likely increased over time. The average concentration of residual non-biodegradable microbial products in the MBR at the end of a typical batch feed cycle was approximately 14 mg/L, as TOC.

The difference in the initial concentration of soluble TOC and the concentration of methanol (expressed as TOC) in the MBR at the start of each batch feed cycle was lower than the residual TOC concentration in the MBR at the end of the preceding batch feed cycle (Figure 7.3). This difference can, in part, be attributed to the dilution effect of adding synthetic evaporator condensate to the MBR at the start of a batch feed cycles. However, less than 2 mg/L of the difference can be attributed to a dilution effect. Much of the remaining difference is likely due to the analytical method used to measure soluble TOC. As presented in Appendix 1, during TOC analysis, the inorganic carbon contained in a sample was removed by acidifying and subsequently purging the inorganic carbon from the sample by stripping it out as CO_2 gas, by bubbling oxygen through the sample. The resulting total carbon content of the sample consisted only of organic carbon. However, the purging step also likely removed some of the volatile methanol from the sample. The amount of volatile TOC stripped from the sample during the purging step is expected to decrease as the concentration of the volatile component of the sample (i.e. the concentration of methanol) decreased. Consequently, the reported concentrations of soluble TOC in the samples collected at the start of the selected batch feed cycles were likely slightly lower than the actual concentrations of soluble TOC in the samples, while the concentrations of soluble TOC in the samples collected later during the selected batch feed cycles, when all of the volatile methanol had been removed, corresponded to the actual concentrations of soluble TOC in the samples. Because of this, it was not possible to determine the rate at which non-biodegradable microbial products were formed. However, it was possible to estimate the total amount of non-biodegradable microbial products formed based on the residual concentration of soluble TOC in the MBR. Based on an approximate mass balance performed on the MBR, approximately 2 % of the influent methanol, expressed as TOC, was converted into soluble non-biodegradable microbial products. The mass balance was based on a flow to the MBR of 4 liters per

day, an influent soluble TOC concentration of 750 mg/L (2000 mg/L as methanol) and a residual soluble TOC concentration of approximately 14 mg/L in the MBR at the end of the batch feed cycle. This is consistent with Chudoba (1985), who reported that the production of non-biodegradable microbial products ranges from approximately 1 to 3.4 % of the substrate consumed for biological systems with an initial substrate to biomass ratio (S_O/X_O) of less than approximately 3. A similar residual concentration, as COD, was reported by Koh et al. (1989) for the biological oxidation of methanol by a mixed microbial culture at a temperature of 30 °C. Further research is required to investigate the rate of non-biodegradable microbial product formation at elevated temperatures.

The formation of non-biodegradable microbial products was not directly investigated when treating real evaporator condensate. However, the formation of non-biodegradable products is expected to be in the same order of magnitude as that observed when treating synthetic condensate, since the TOC loading rate to the MBR was in the same order of magnitude in both experiments (Chudoba, 1985). Since some non-biodegradable microbial products are formed during treatment, the actual reduction in the concentration of TOC initially present in the evaporator condensate was higher than the observed value of 91%. Assuming that a non-biodegradable microbial product formation is approximately 2 % of the initial TOC, as observed when treating synthetic evaporator condensate, the actual reduction in the concentration of TOC initially present in the evaporator condensate was estimated to be approximately 93%.

7.4 Fate of Reduced Sulphur Compounds During Treatment

This section discusses the results obtained from the investigation of the fate of RSC contained in evaporator condensate during treatment using a high temperature MBR. The raw data, on which this discussion is based, are presented in Appendix 7.

All of the RSC were removed from the evaporator condensate before the end of each batch feed cycle. The concentrations of RSC in the feed to the MBR were lower than the concentration of these RSC in the evaporator condensate from the mill as presented in Appendix 2. The reduction in their concentrations was due to the degradation of these relatively unstable compounds during storage of the evaporator condensate. The concentrations of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide in the MBR were reduced from approximately 12.6, 32.5, 19.0 and 4.4, respectively (characteristics of feed to the MBR), to below detection limits of approximately 0.4 mg/L. However, all of the RSC were also removed when the biomass was inactivated, indicating that the removal of RSC could be attributed to abiotic processes. This was similar to the results obtained during the feasibility experiment that suggested that the removal of dimethyl sulphide and dimethyl disulphide was due to stripping by the aeration system (Chapter 4). To investigate the fate of the RSC contained in evaporator condensate during high temperature biological treatment using an MBR, a mass balance calculation was performed around the MBR.

All of the methyl mercaptan contained in the influent evaporator condensate was removed from the MBR before the end of the 60-minute mass balance monitoring period. Methyl mercaptan is very volatile under the conditions present in the MBR. However, only a relatively small amount of the methyl mercaptan contained in the influent was stripped and recovered with the off-gas. Approximately 33 % (corrected value based on capture efficiency of RSC traps) of the methyl mercaptan removed from the MBR was recovered with the off-gas. The capture efficiency of the traps for the different RSC is discussed in Appendix A1.4. A similar amount of methyl mercaptan was recovered with the off-gas when the biomass was inactivated, suggesting that methyl mercaptan was rapidly abiotically oxidized in the MBR before it could be stripped by the aeration system.

When the MBR was fed real evaporator condensate, approximately 422 % (corrected value based on capture efficiency of RSC traps) of the dimethyl disulphide removed from the MBR was recovered with the off-gas. However, when synthetic evaporator

condensate (containing only methanol, dimethyl sulphide and dimethyl disulphide) was used as feed, approximately 100 % (corrected value based on capture efficiency of RSC traps) of the dimethyl disulphide removed from the MBR was recovered with the off-gas. The different amounts of dimethyl disulphide recovered with the off-gas, when real and synthetic evaporator condensates were used as feed are illustrated in Figure 7.4. The cumulative fraction of dimethyl disulphide recovered increased linearly over time when synthetic evaporator condensate was used as feed. When real evaporator condensate was used as feed, the cumulative fraction of dimethyl disulphide recovered was similar to that observed when using synthetic evaporator condensate at the end of the first 15 minutes of the mass balance monitoring period. However, as illustrated in Figure 7.4, after approximately 15 minutes, the cumulative fraction of dimethyl disulphide in the off-gas increased rapidly. This suggests that dimethyl disulphide, in excess of what was originally present in the influent real evaporator condensate, was recovered in the RSC traps. This is consistent with results reported by Saunders (1995). In developing an analytical method for measuring the concentration of RSC in aqueous solutions, Saunders (1995) observed that aqueous methyl mercaptan can oxidize abiotically to dimethyl disulphide. Assuming that the additional recovered dimethyl disulphide was formed from the oxidation of methyl mercaptan, approximately 29 % of the methyl mercaptan contained in the influent was oxidized and recovered as dimethyl disulphide. With this assumption, approximately 62 % of the methyl mercaptan contained in the influent to the MBR was accounted for during the mass balance. Further research is required to confirm the fate and oxidation kinetics for methyl mercaptan during treatment using a high temperature MBR.

All of the hydrogen sulphide contained in the influent evaporator condensate was also removed from the MBR before the end of the 60-minute mass balance monitoring period. Hydrogen sulphide is very volatile under the conditions present in the MBR. However, of the hydrogen sulphide removed from the MBR, only approximately 3 % was recovered with the off-gas. As discussed in Appendix A1.4, the capture efficiency of the RSC traps for hydrogen sulphide was poor (capture efficiency of approximately 5 %). Therefore, it is not possible to draw any conclusions from the amount of hydrogen

sulphide recovered in the RSC traps. However, there was no odor, characteristic of that for hydrogen sulphide, present in the off-gas vented to the atmosphere downstream of the RSC traps. This suggested that the vented off gas did not contain any hydrogen sulphide. The absence of a hydrogen sulphide odor in the off-gas vented to the atmosphere suggests that the non-recovered portion was rapidly oxidized in the MBR before it was stripped by the aeration system. However, because of the rapid and complete removal of hydrogen sulphide from the MBR as well as the poor capture efficiency of the RSC traps for hydrogen sulphide it was not possible to determine if the removal of hydrogen sulphide was due predominantly to biological or abiotic mechanisms. Nonetheless, abiotic oxidation is expected to contribute substantially to the removal of hydrogen sulphide from the MBR. Chen and Morris (1972) and Wilmot et al. (1988) reported that aqueous hydrogen sulphide can be rapidly abiotically oxidized to sulphate in the presence of oxygen at a neutral pH as maintained in the MBR. Mahmood et al. (1999) reported that trace metals, such as those contained in the nutrient solution added to the MBR, can catalyze the abiotic oxidation of hydrogen sulphide. Their studies indicated that over 500 mg/L of hydrogen sulphide can be abiotically oxidized within a few minutes at conditions present in biological wastewater treatment systems. Unfortunately, it was not possible to accurately monitor the production of sulphate from the oxidation of hydrogen sulphide in the MBR due of the relatively high concentration of sulphate in the nutrient solution added to the MBR (Appendix 3) and the relatively low concentration of hydrogen sulphide in the evaporator condensate. Consequently, only approximately 3 % of the hydrogen sulphide contained in the influent to the MBR was accounted for during the mass balance. Further research is required to determine the fate and oxidation kinetics for the non-recovered portion of the influent hydrogen sulphide during treatment using a high temperature MBR.

Approximately 100 % (corrected value based on capture efficiency of RSC traps) of the dimethyl sulphide removed from the MBR was recovered with the off-gas. This indicates that the removal of dimethyl sulphide was entirely due to stripped during treatment due to the aeration system. This is consistent with the results observed during the feasibility experiment (Chapter 4). Based on the concentrations of dimethyl disulphide in the MBR

at the start and end of the mass balance monitoring period, the first order coefficient for the stripping of dimethyl sulphide was estimated to be approximately 0.033 /minute.

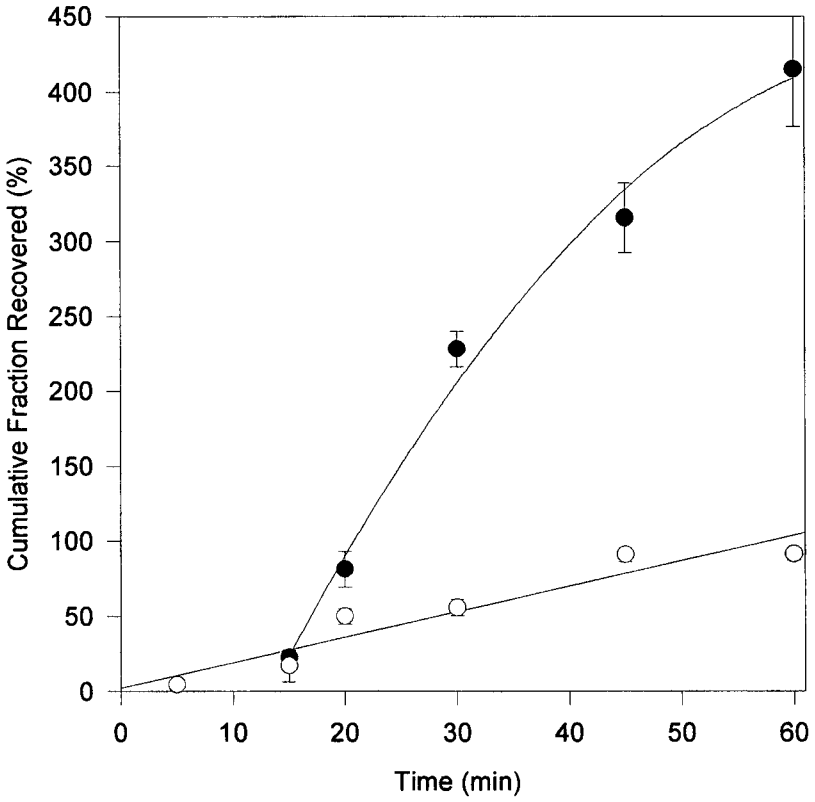


Figure 7.4 – Cumulative Fraction of Dimethyl Disulphide Recovered in RSC Traps (solid symbols: real evaporator condensate as feed; open symbols: synthetic evaporator condensate as feed; error bars represent 90 % confidence interval of measurements)

In the absence of methyl mercaptan (when using synthetic evaporator condensate), similar results to those observed for dimethyl sulphide were also observed for dimethyl disulphide, indicating that dimethyl disulphide was also entirely stripped with the off-gas due to the aeration system. Again, this is consistent with to the results observed during the feasibility experiment (Chapter 4). Based on the concentrations of dimethyl sulphide in the MBR at the start and end of the mass balance monitoring period, when using

synthetic evaporator condensate as feed, the first order coefficient for the stripping of dimethyl disulphide was estimated to be approximately 0.021 /minute.

These results suggest that methyl mercaptan and hydrogen sulphide were rapidly oxidized in the mixed liquor contained in the high temperature MBR. To minimize the amount of these RSC that are stripped to the atmosphere due to the aeration system and to maximize the amount that is oxidized, the head-space in the MBR could be recycled back into the mixed liquor. This could increase the amount of these RSC that are abiotically oxidized. However, further research is required to determine the optimal operating parameters to maximize the abiotic oxidation of methyl mercaptan and hydrogen sulphide in a high temperature MBR treating evaporator condensate.

As an alternative, the RSC contained in the off-gas from a high temperature biological treatment system could be oxidized using a designated catalytic incinerator or a biofilter. The off-gas could also be hard-piped to an existing power or recovery boiler for incineration. The incineration of RSC in the power or recovery boiler could also potentially reduce the overall dioxin emissions from a kraft pulp mill (Uloth, 1999).

7.5 Summary

A summary of the fate of the contaminants of concern present in the evaporator condensate, during high temperature biological treatment using an MBR is presented in Table 7.1.

These results indicate that a high temperature biological treatment system can be used to successfully remove the contaminants of concern from evaporator condensate.

1. As discussed in Chapter 6, over 99 % of the methanol contained in the real evaporator condensate could be biologically removed during high temperature biological

treatment. The concentration of methanol in the evaporator condensate was reduced from approximately 964 ± 272 mg/L to below detection limits (approximately 0.5 mg/L). Approximately 2 % of the methanol removed was converted to non-biodegradable microbial products. The specific methanol utilization coefficient was estimated to be 0.59 ± 0.11 /day when treating real evaporator condensate.

Table 7.1 - Summary of Fate of the Contaminants of Concern Contained in Evaporator Condensate During High Temperature Biological Treatment Using an MBR

(mg/L as TOC; n.d.: non-detectable)

Influent 504 mg/L			Processes Occuring in Membrane Bioreactor	Effluent 52 mg/L
Organic Contaminants	Other Organics	Particulate	Potential refractory compounds (removed with waste sludge) Hydrolyzed to soluble products	(n.d.)
		Soluble	Potential refractory compounds Biodegradable compounds consumed as substrate Some refractory microbial products formed	52 mg/L
	Methanol		91 % Oxidized to carbon dioxide and water 9 % Synthesized to biomass Some refractory microbial products formed	(n.d.)
	Reduced Sulphur Compounds	DMS	> 99 % Stripped with off-gas	(n.d.)
		DMDS	> 99 % Stripped with off-gas	(n.d.)
		CH3SH	Abiotically oxidized (some to DMDS) 33 % Stripped with off-gas	(n.d.)
H2S		H2S	Abiotically Oxidized 3 % Stripped with off-gas	(n.d.)

(Influent: concentration of contaminants in evaporator condensate feed to the MBR; Effluent: concentration of contaminants in MBR at the end of the 3-hour batch feed cycle)

2. Approximately 93 % of the organic compounds, measured as TOC, contained in the evaporator condensate could be removed during high temperature biological treatment. The observed TOC removal efficiency was approximately 91%. The difference between the observed and actual TOC removal efficiency was due to the formation of non-degradable microbial products by the mixed culture during treatment. The removal of methanol accounted for approximately 78 % of the TOC removed. The concentration of TOC in the evaporator condensate was reduced from 504 ± 137 mg/L to 52 ± 3.6 mg/L. The specific TOC utilization coefficient was estimated to be 0.66 ± 0.056 /day.

3. Over 99% of the RSC were removed from the evaporator condensate using a high temperature MBR. The concentrations for hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl sulphide were reduced to below detection limits (approximately 0.4 mg/L), during high temperature biological treatment using an MBR. The results suggest that up to approximately 67 and 97 % of the influent methyl mercaptan and hydrogen sulphide, respectively, were abiotically oxidized in the MBR. The remaining fractions were stripped from the MBR due to the aeration system. Dimethyl sulphide and dimethyl disulphide were completely removed from the evaporator condensate during treatment by stripping due to the aeration system.

Chapter 8 – Conceptual Design and Cost Estimates for a Full-Scale High Temperature MBR for the Treatment of Evaporator Condensate for Reuse

8.1 Introduction

As outlined in Chapter 1, the objective of this study was to improve our understanding of the physical, chemical and biological processes that occur during the high temperature biological treatment of evaporator condensate. The evaporator condensate used during the study was characterized and the contaminants of concern were identified. The fate and removal kinetics of these contaminants of concern, during high temperature biological treatment, were investigated. Achievable contaminant removal efficiencies were determined. The operating temperature for the optimal removal of the methanol was identified. This information was required to develop a conceptual design for a full-scale high temperature MBR for the treatment of evaporator condensate for reuse. A conceptual design of a high temperature MBR to treat evaporator condensate for reuse is presented in this Chapter. Only the treatment of the evaporator condensate (foul fraction of the evaporator condensate) was considered. As discussed in Section 2.1, the clean fraction of the evaporator condensate was considered to be sufficiently clean to be reused directly without treatment. Based on the design, capital and operating costs were estimated. To determine the economic feasibility of biologically treating evaporator condensate for reuse using a high temperature MBR, the costs associated with a high temperature MBR were compared with the costs associated with a steam stripping system capable of achieving a similar treatment efficiency. A steam stripping system is considered by some as the most attractive conventional technology to treat evaporator condensate for reuse.

8.2 Design Parameters

The design parameters were determined based on the results obtained from experiments 1 through 4, as presented in Chapters 4 to 7. The design parameters are presented in the following sections and are summarized in Table 8.1.

Table 8.1 – Summary of Design Parameters

Design Parameters	Value
Evaporator Condensate Characteristics	
Flow (m^3/minute)	0.6
Methanol (mg/L)	1200
Total Organic Carbon (mg/L)	640
Hydrogen Sulphide (mg/L)	110
Methyl Mercaptan (mg/L)	120
Contaminant Removal Efficiency	
MBR	
Methanol (%)	99
Total Organic Carbon (%)	90
Hydrogen Sulphide (%)	99
Methyl Mercaptan (%)	99
Steam Stripper	
Methanol (%)	90
Hydrogen Sulphide (%)	99
Methyl Mercaptan (%)	99
Contaminant Removal Kinetics	
Specific Methanol Utilization Coefficient (/day)	0.59
Specific TOC Utilization Coefficient (/day)	0.66
Non-Degradable TOC (mg/L)	52
Observed Growth Yield (mg/mg)	0.2
Operating Temperature (°C)	60
MLVSS Concentration (mg/L)	10000

Characteristics of the Evaporator Condensate to be Treated

As presented in Chapter 2, organic compounds and RSC were identified as the primary contaminants of concern. More specifically, methanol, various organic compounds, hydrogen sulphide and methyl mercaptan were identified as the contaminants of concern. The high temperature MBR was designed to treat evaporator condensate with characteristics similar to those observed at the Western Pulp Limited Partnership bleached kraft pulp mill in Squamish, Canada (Appendix 2). The assumed characteristics of the evaporator condensate to be treated were based on the upper limit of the 90 % percentile of the measurements made for the concentrations of the contaminants of concern. The evaporator condensate flow selected was based on the foul evaporator condensate flow measured at the Western Pulp mill. The characteristics of the evaporator condensate used for the conceptual design are listed in Table 8.1.

Contaminant Removal Efficiencies

As discussed in Chapter 7, a 99% removal efficiency for methanol and a 90 % removal efficiency for organic contaminants, measured as TOC, contained in the evaporator condensate can be easily achieved during high temperature biological treatment. Also, virtually all of the hydrogen sulphide and methyl mercaptan can be removed from the evaporator condensate during biological treatment as presented in Chapter 7. Since a high temperature MBR proved to be very efficient for removing the contaminants of concern, high contaminant removal efficiencies were assumed for the design of the full-scale high temperature MBR. The design removal efficiencies selected for methanol, TOC and RSC (as hydrogen sulphide and methyl mercaptan) were 99, 90 and 99 %, respectively.

Steam stripping systems are generally capable of removing approximately 90 % of the methanol contained in evaporator condensate (Vora and Venkataraman, 1995; NCASI, 1994b; Zuncich et al., 1993). Achieving a higher methanol removal efficiency is considered to be prohibitively expensive (Vora and Venkataraman, 1995). Also, organic

carbon removal efficiencies have been reported to be 47 to 97 % of the removal efficiencies for methanol (Danielsson and Hakansson, 1996). For comparison purposes, a steam stripper system capable of achieving a 90 % methanol removal efficiency was designed. The design RSC removal efficiency was 99 %.

The design contaminant removal efficiencies are summarized in Table 8.1.

Contaminant Removal Kinetics

The contaminant removal kinetics measured for an operating temperature of 60 °C were selected for the design of the full-scale high temperature MBR. As presented in Chapter 6, methanol was observed to follow a zero order removal rate in the MBR. The estimated specific methanol utilization coefficient was 0.59 /day. As presented in Chapter 7, TOC was observed to follow a first order removal rate based on the biodegradable fraction of the TOC in the MBR when treating evaporator condensate. The concentration of the non-biodegradable fraction of the TOC in the MBR when treating evaporator condensate was approximately 52 mg/L. The estimated specific TOC utilization coefficient was 0.66 /day.

The design contaminant removal rates are summarized in Table 8.1.

Other Operating Parameters

An operating temperature of 60 °C was selected. As presented in Chapter 5, the maximum specific methanol utilization coefficient was observed at this temperature.

To estimate biomass production, an observed growth yield of 0.2 mg MLVSS produced/mg methanol biologically removed was selected. This corresponds to the observed growth yield measured when treating real evaporator condensate (Chapter 6).

An MLVSS concentration of 10000 mg/L, which corresponds to the lower range of commonly achievable concentrations in an MBR as discussed in Section 2.3.4, was selected to generate a conservative design.

8.3 Conceptual Design

Based on the design parameters presented in Table 8.1, the reactor tank, the aeration system and the ultrafiltration membrane system were sized.

Reactor Tank

The reactor tank component of the MBR was sized based on the largest tank size required to remove methanol and other organic contaminants (as TOC). The reactor tank component of the MBR was designed as a plug flow reactor (PFR). A PFR design was selected to minimize the reactor tank volume required to achieve 90 % TOC removal as discussed below.

The hydraulic residence time required to remove methanol from the evaporator condensate can be calculated by solving Equation 4.4 for a PFR as presented in Equation 8.1:

$$\Delta_{MEOH} = \frac{C_O - C_E}{U_{MeOH} X} \qquad (8.1)$$

where θ_{MEOH} is the required hydraulic retention time to remove methanol (day), C is the concentration of methanol (mg/L), subscript O corresponds to the design influent concentration, subscript E corresponds to the design effluent concentration, U_{MeOH} is the design specific methanol utilization coefficient (/day) and X is the design MLVSS concentration (mg/L).

Based on the design parameters, a hydraulic retention time of approximately 5 hours is required to achieve 99 % methanol removal efficiency. This corresponds to a reactor size of approximately 180 m^3.

Similarly, the reactor tank size required for TOC removal can be calculated by solving Equation 7.6 for a PFR as presented in Equation 8.2:

$$\Delta_{TOC} = \frac{\ln\left(\frac{S_E - S_N}{S_O - S_N}\right)(S_O - S_N)}{U_{TOC}X} \qquad (8.2)$$

where θ_{TOC} is the required hydraulic retention time to remove TOC (day), S is the TOC concentration (mg/L), U_{TOC} is the design specific TOC utilization coefficient (/day) and subscript N corresponds to the design non-degradable component.

Based on the design parameters, a hydraulic retention time of approximately 8.3 hours is required to achieve 90 % TOC removal efficiency. This corresponds to a reactor size of approximately 300 m^3. Had the MBR been designed as a continuous stirred tank reactor (CSTR) instead of a PFR, a hydraulic retention time of approximately 4.2 days would have been required to achieve a 90 % TOC removal efficiency.

The larger of the required hydraulic retention times, 8.3 hours, was selected for the design of the reactor tank component of the MBR.

The removal rates for hydrogen sulphide and methyl mercaptan were not determined directly. However, based on the mass balance presented in Section 7.4, virtually all of the hydrogen sulphide and the methyl mercaptan contained in the evaporator condensate were removed from the MBR within 60 minutes. Consequently, for the selected design hydraulic residence time of 8.3 hours, all of the hydrogen sulphide and methyl mercaptan should be removed from the evaporator condensate during treatment.

The loading rate to the MBR based on a hydraulic residence time of 8.3 hours is more than twice that used during the present study when treating real evaporator condensate (Section 6.2). Therefore, an MLVSS concentration of approximately twice that observed during the present study, which corresponds to a MLVSS concentration of 5500 mg/L, can be expected in the MBR. A MLVSS concentration of 5500 mg/L is much lower than that selected for the design of the MBR. However, it is possible to increase the MLVSS concentration by reducing the sludge wastage rate from the MBR. For the selected design observed growth yield of 0.2, it may be possible to maintain an MLVSS concentration of 10000 mg/L by increasing the sludge retention time from 20 days to approximately 38 days. It should be noted that increasing the sludge retention time may reduce the observed growth yield (Metcalf and Eddy, 1991). The effect of the sludge retention time on the observed growth yield was not investigated during the present study. Further research is required to determine the effect of the sludge retention time on the observed growth yield.

Aeration System

It was not possible to accurately determine the air requirements for an MBR treating evaporator condensate for reuse based in the data collected. For the purpose of the conceptual design, the aeration requirements were estimated based on the oxygen required to fully oxidize the methanol contained in the evaporator condensate. An aeration system with an oxygen transfer efficiency (OTE) of 20 % was assumed (fine bubble diffuser system). Methanol accounted for approximately 70 % of the TOC contained in the evaporator condensate. To account for the air requirements for the oxidation of non-methanolic organic compounds, the air requirements were increased by 30 % (see Appendix 8). Based on these assumptions, the amount of air required was estimated to be approximately 32 m^3/minute. This corresponds to a volumetric aeration rate of 0.11 m^3 of air/m^3•minute of reactor volume. This volumetric aeration rate is approximately half of that which was required to maintain non-limiting dissolved oxygen conditions in the small bench scale MBR during the present study when treating real evaporator condensate. The OTE in a biological treatment system increases with the

depth of submergence of the aeration system (Metcalf and Eddy, 1991). Typically, the OTE for fine bubble diffusers, such as those used in the small bench scale MBR and the conceptual design, increases by approximately 3 to 5 % for each meter of submergence. Considering that the small bench scale MBR had a depth of submergence of approximately 40 cm and the conceptual design of the full scale MBR has a submergence of 10 m, the OTE in the full scale system is expected to be substantially higher than for the small bench scale MBR. Therefore, the design aeration rate of 32 m^3/minute should be sufficient to provide non-limiting dissolved oxygen conditions in the full scale MBR.

The power required to deliver 32 m^3/minute of air, estimated as presented in Metcalf and Eddy (1991), was approximately 39 kW. For the selected reactor tank volume of 300 m^3 and a mixed liquor temperature of 60 °C, a power input of 39 kW by the aeration system should completely mix in the reactor tank contents (Metcalf and Eddy, 1991). Therefore, baffles will have to be installed in the reactor tank component of the MBR to prevent completely mixed conditions in the tank and promote plug flow conditions.

The aeration system design and the aeration rate will affect the abiotic removal of RSC. However, the selected design hydraulic retention time of 8.3 hours should provide sufficient time for the RSC to be removed abiotically.

Ultrafiltration System

A pseudo steady state permeate flux of 162 L/hour•m^2 was maintained in the ultrafiltration membrane component of the small bench scale MBR used during the present study when treating real evaporator condensate. However, as discussed in Section 2.3.4, the steady state permeate flux has been reported to decrease at higher MLVSS concentrations (Cheryan, 1986). According to Magara and Itoh (1991) and Shimizu et al. (1993), increasing the MLVSS concentration from approximately 2400 mg/L, as observed during the present study, to 10000 mg/L, as selected for the conceptual design of the full scale MBR, should decrease the steady state permeate flux by approximately 50 % (assuming all other operating parameters are the same for the small

bench scale MBR used during the present study and the conceptual design of the full scale MBR). Fortunately, this decline can be offset by adjusting a number of operating parameters. The cross-flow velocity over the surface of an ultrafiltration membrane component of an MBR typically ranges from 3 to 5 m/s (personal communication, Johnson H., 1999, US Filters, USA). Operating at a lower cross-flow velocity results in excessively low permeate fluxes while operating at higher cross-flow velocities can produce excessive shear resulting in reduced biological activity in the MBR (Flaschel et al., 1986). As discussed in Section 2.3.4, the steady state permeate flux increases linearly with the cross-flow velocity (Shimizu et al., 1991; Magara and Itoh, 1991). The cross-flow velocity that was maintained in the small bench scale MBR used during the present study was approximately 3 m/s. It would be possible to increase the steady state permeate flux by almost 70 % by increasing the cross-flow velocity to 5 m/s. Furthermore, it could also be possible to increase the steady state permeate flux by increasing the trans-membrane pressure (Cheryan, 1986). The trans-membrane pressure in an utrafiltration membrane component of an MBR typically ranges from 1 to 4 atmospheres (personal communication, Johnson H., 1999, US Filters, USA). The trans-membrane pressure that was maintained in the small bench scale MBR used during the present study was approximately 2 atmosphere (30 psi). Further tests would be required to determine the optimal operating set points and the maximum achievable pseudo steady state permeate flux for the membrane component of the MBR. Nonetheless, it appears that the negative impact of a higher MLVSS on the steady state permeate flux can be overcome by adjusting a number of operating parameters.

For the conceptual design of the membrane component of the MBR, the pseudo steady state permeate flux maintained in the ultrafiltration membrane component of the small bench scale MBR during the present study when treating real evaporator condensate was selected. This corresponded to a permeate flux of approximately 162 L/hour•m^2 of membrane area. A permeate flux of 162 L/hour•m^2 is typical of MBR applications (personal communication, Johnson H., 1999, US Filters, USA). For a flow of 0.6 m^3/minute, a membrane surface area of 223 m^2 is required. A cross-flow velocity of 5 m/s was also selected for the conceptual design.

8.4 Capital and Operating Cost Estimates

Capital Costs

The capital cost estimate included equipment, installation, piping, electrical, instrumentation, civil works, engineering, contractor overhead/profits and contingency. Taxes were not included. All costs are expressed in Canadian dollars. A generic capital cost is difficult to estimate because of variations in mill size and layout. To ensure an adaptable capital cost estimate, the following assumptions were made (Barton et al, 1996).

1. Evaporator condensate to be treated would be collected in storage tanks.
2. Evaporator condensate would be piped approximately 300 meters to the treatment system and the treated evaporator condensate would be piped approximately 300 meters to the point of reuse.
3. The treated evaporator condensate would be collected in a treated condensate storage tank.
4. Waste sludge would be piped approximately 150 meters to an existing secondary treatment system.
5. Vent gases would be piped approximately 150 meters to an existing power boiler or lime kiln for incineration.
6. Steam would be piped approximately 300 meters to the stripper system.
7. No cooling would be required.

The waste sludge would be processed along with the waste sludge produced by the existing combined mill effluent secondary treatment system. The amount of waste sludge produced by a high temperature MBR treating evaporator condensate for reuse is expected to be similar to the amount of waste sludge produced if the evaporator condensate is treated in the combined mill effluent secondary treatment system. Therefore, no additional sludge handling costs are expected for treating evaporator condensate for reuse using a high temperature MBR.

The capital cost for the MBR system was estimated based on equipment quotes for each of the MBR components (stainless steel tank, aeration system, ultrafiltration membrane system, pumps, piping and instrumentation). The capital cost estimate for treating evaporator condensate for reuse, using a high temperature MBR, is summarized in Table 8.2. Quotes and cost estimates are presented in Appendix 8.

The membrane costs listed in Table 8.2 are for ceramic ultrafiltration membranes, similar to those used in the present study. The costs for the ceramic membrane were based on discussions with the membrane supplier for a system with a total area of 223 m^2 (US Filers, USA). Ceramic ultrafiltration membranes have a proven track record for operating under harsh conditions such as elevated temperatures. However, they tend to be more expensive than polymeric membranes. With recent developments in membrane materials, it may be possible to use hollow fiber polymeric membranes at operating temperatures of 60 °C. Using submerged hollow fiber polymeric membranes in the MBR system would reduce the capital cost associated with the membrane component by almost 50 %, as well as reducing the operating power requirements. The costs for the polymeric membrane were provided by the polymeric membrane supplier based on the design parameters listed in Table 8.1 (the membrane supplier requested anonymity). The design calculations were not available since they were considered to be proprietary information. Using polymeric membranes, the resulting overall costs would be significantly less, as presented in Tables 8.2 and 8.3. The major disadvantage associated with using submerged hollow fiber membranes is that their long term use at elevated temperatures has not been well documented.

The capital cost for the steam stripping system was estimated based on delivered and installed cost for complete steam stripper systems, provided by established consulting firms and equipment suppliers. The capital cost estimates include all steam stripper components (pumps, motors stripping column and instrumentation). Steam stripper capital costs obtained from two independent suppliers were in the same order of magnitude. The capital cost estimates for treating the evaporator condensate for reuse are presented in Table 8.2.

Table 8.2 - Capital Cost Estimates

(Thousands $)

Cost Component	Cost
Membrane Bioreactor	
Piping	500
Storage Tanks & Pumps	180
Chemical Addition	65
MBR Tank	175
Aeration System	1,100
Membranes	1,300
	(*600)
Civil/Electrical	660
TOTAL	**$3,980**
	(*$3,280)
Steam Stripping	
Yard Piping	500
Storage Tanks and Pumps	180
Steam Stripper	4,800
Kiln Combustion System	200
Civil/Electrical	660
TOTAL	**$6,280**

(*total cost for MBR system using polymeric membranes)

A safety factor of 30 to 50 % is typically used in the design of the reactor tank component of a biological treatment system. However, as presented in Bérubé and Hall (2000), increasing the size of the reactor tank by 30 to 50 % would not increase total capital cost of a high temperature MBR by a significant amount. There is typically no, or a relatively small safety factor (less than 10 %) used in the design of steam strippers (personal communication, Bruce D., Simons, Vancouver, Canada). This is because the use of steam strippers to treat evaporator condensate has been thoroughly investigated

(McCance and Burke, 1980; NCASI, 1994b). Since a safety factor is not required (for the steam stripping system) or would not significantly affect the estimated capital cost (for the MBR), a safety factor was not used in the conceptual design of the high temperature MBR and a steam stripper to treat evaporator condensate for reuse.

Operating Costs

The operating cost estimates for the MBR system are summarized in Table 8.3. The costs are expressed per air dried metric tonne of pulp produced (ADMT). The pulp production at the Western Pulp Limited Partnership mill is 816 ADMT per day. Operating cost calculations are presented in Appendix 8. The electrical operating costs were estimated based on $0.1 /kWh. Equipment maintenance and replacement costs were estimated based on a yearly operating cost equivalent to 2 % of the installed equipment costs (Barton et al.,1996). The chemical operating costs were adapted from Barton et al. (1996) based on biochemical oxygen demand (BOD) removal. The labor cost is for four full-time personnel equivalents (Barton et al.,1996).

The operating cost estimates for the steam stripper system are also listed in Table 8.3. The cost associated with steam generation is highly mill specific and is function of existing steam generating capacity. Based on discussions with local engineering consultants, the cost of providing steam was estimated based on a life cycle cost for a large boiler, fired with gas and wood waste fuel, over a 20 year period. Given local conditions and 9 % financing, the life cycle cost of providing steam is estimated to be $5/1000 lb ($11/1000 kg) steam. Fuel credits are based on a fuel value of 22,700 kJ/kg for methanol and a fuel cost of $3.5/GJ (CANMET, 1994). Labor and equipment maintenance costs were estimated as described above.

As an alternative, waste heat from a blow heat recovery system could be used to meet the steam requirements for the stripper system (Hough and Sallee, 1977; Farr et al., 1993). This could reduce the operating cost for steam by as much as one order of magnitude (Farr et al., 1993). However, significant modifications to existing mill equipment would

be required (NCASI, 1994b). Consequently, waste heat recovery for steam stripping may only be feasible with new mills.

Table 8.3 - Operating Cost Estimates

(per ADMTP)

Cost Component	Cost
Membrane Bioreactor	
Power	
Membrane	0.34
	(*0.06)
Aeration System	0.12
Chemicals	0.25
Labor	0.60
Equipment	0.05
TOTAL	**$1.36**
	(*1.08)
Steam Stripping	
Steam	2.32
Fuel Economy	-0.10
Labor	0.60
Equipment	0.15
TOTAL	**$2.97**

(*total cost for MBR system using polymeric membranes)

8.5 Cost Comparison

The capital cost estimates indicate that biological treatment, using a high temperature MBR, could be significantly less expensive than steam stripping, when treating evaporator condensate for reuse. Depending on the type of membranes used in the MBR design, the capital cost for the MBR system was approximately 40 to 50 % less than the

capital cost of a steam stripping system capable of achieving comparable contaminant removal efficiencies. Given local conditions and 9 % financing over a 20 year period, the capital cost of an MBR and a steam stripping system to treat evaporator condensate are $1.45 /ADMT ($1.18 /ADMT if polymeric membranes can be used) and $2.27 /ADMT, respectively.

The operating cost of an MBR system was less than half than that for a steam stripping system. This is similar to previously published cost estimates. Garner (1996) reported that the annual cost for a steam stripping system for methanol removal was more than twice that for a conventional aerobic biological treatment system. Vora and Venkataraman (1995) also indicated that the operating cost associated with generating steam can be prohibitively expensive when steam stripping large flows. The operating cost for an MBR could be even lower if hollow fiber polymeric membranes can be used at elevated temperatures.

The total costs of treating evaporator condensate for reuse using an MBR and a steam stripping system are $2.81 /ADMT ($2.26 /ADMT if polymeric membranes can be used) and $5.24 /ADMT, respectively.

The cost estimate for the MBR indicated that the capital cost is most sensitive to the volume of wastewater to be treated and not the required contaminant removal efficiency (Bérubé and Hall, 2000). Therefore, achieving high methanol and TOC removal efficiencies, as in the present conceptual design, does not substantially affect the total capital cost.

The above cost comparison assumes that the two systems are capable of removing the contaminants of concern from the evaporator condensate to similar levels. However, as discussed in Section 8.2, it is prohibitively expensive to use a steam stripping system to achieve a 99 % methanol removal efficiency as was selected for the conceptual design of the high temperature MBR. Therefore, it is not only more expensive to treat evaporator condensate for reuse using a steam stripping system, but it is also not economically

feasible to achieve treatment efficiencies comparable to that of a high temperature MBR with a steam stripping system.

8.6 Summary

Based on assumed removal efficiencies of 99, 90 and 99 % for methanol, TOC and RSC (as hydrogen sulphide and methyl mercaptan), respectively, as well as the characteristics of the evaporator condensate from a local kraft pulp mill, a conceptual design for a full-scale high temperature MBR to treat evaporator condensate for reuse was developed. Capital and operating costs were estimated and compared to the costs for a steam stripping system capable of achieving similar treatment efficiencies. Depending on the type of ultrafiltration membranes used in the MBR design, the capital cost for the MBR system was 40 to 50 % less than the capital cost of a steam stripping system capable of achieving comparable contaminant removal efficiencies. The operating costs for the MBR system were also approximately 50 % less than the operating costs for a steam stripping system. Therefore, high temperature biological treatment is not only technically feasible, as presented in Chapters 4 to 7, but is also economically more attractive than the currently favored treatment technology (i.e. steam stripping).

Chapter 9 – Conclusions, Significance of Results to Environmental Process Engineering and Recommendations for Further Studies

9.1 Conclusions and Significance of Results to Environmental Process Engineering

Feasibility of Biologically Removing Methanol and Reduced Sulphur Compounds from Evaporator Condensate at an Elevated Temperature

The first experiment, presented in Chapter 4, investigated the feasibility of biologically removing methanol and reduced sulphur compounds from synthetic evaporator condensate at an elevated temperature. The major conclusions from the feasibility experiment were as follows.

1. Biological removal of methanol in a high temperature MBR is feasible. It was possible to grow a mixed microbial culture capable of biologically oxidizing the methanol contained in synthetic evaporator condensate at a temperature of 55 °C.

2. Over 99 % of the methanol contained in the synthetic evaporator condensate was biologically removed during treatment. The observed specific methanol utilization coefficient of 0.72 ± 0.11 /day was higher than the values previously reported by others for the biological treatment of real evaporator condensate at a much lower temperature.

3. Over 99 % of the RSC contained in the synthetic evaporator condensate was removed in the high temperature MBR. However, at a neutral pH, as required for the growth of a mixed culture of methanol-consuming microorganisms, the removal of the RSC was due to stripping by the aeration system. A pH of less than approximately 4 was required for the biological oxidation of RSC to occur. However, even at a pH of 3, which is reported by others to be the optimal pH for the growth of thermophilic

sulphur-oxidizing microorganisms, stripping still accounted for approximately 50 % of the removal of RSC from the synthetic evaporator condensate. The biological oxidation of methanol was significantly inhibited at a pH of less than approximately 5.

The results from the first experiment indicated that methanol can be removed from evaporator condensate using high temperature biological treatment. The results also suggested that high temperature biological treatment can potentially be more efficient than a conventional biological treatment.

However, the results from the feasibility experiment also indicated that a low pH is required for the biological oxidation of RSC to occur. Biological methanol removal was significantly inhibited at the low pH required for biological RSC removal to occur. Therefore, the simultaneous biological removal of methanol and RSC from evaporator condensate using a high temperature biological treatment system is not feasible. A two-stage system, with the first stage operating at an acidic pH for the biological removal of RSC and a second stage operating at a neutral pH for the biological removal of methanol, would be required. However, a two-stage system would significantly increase the cost associated with the treatment of evaporator condensate for reuse. In addition, a significant amount of RSC would still be stripped due to the aeration system. For these reasons, the biological removal of RSC was not considered to be feasible.

As an alternative to the biological oxidation of the RSC contained in the evaporator condensate, the off-gas from a high temperature biological treatment system could be treated using a designated catalytic incinerator or a biofilter. The off-gas could also be hard piped to an existing power or recovery boiler for incineration. The incineration of RSC in the power or recovery boiler could potentially also reduce the overall dioxin emissions from a kraft pulp mill (Uloth, 1999).

Effect of Operating Temperature on the Biological Removal of Methanol

The second experiment, presented in Chapter 5, investigated the effects of the operating temperature on the biological removal of methanol from synthetic evaporator condensate at operating temperatures ranging from 55 to 70 °C. The temperature range investigated corresponds to the expected range for the evaporator condensate stream. The major conclusions from the experiment investigating the effect of the operating temperature are as follows.

1. It was possible to grow a mixed microbial culture capable of biologically oxidizing the methanol contained in synthetic evaporator condensate at temperatures ranging from 55 to 70 °C.

2. The origin of the inoculum used did not have a significant impact on the mixed microbial culture in the high temperature MBR.

3. The operating temperature exerted a significant effect on methanol removal kinetics. The specific methanol utilization coefficient and the specific growth coefficient increased to a maximum of 0.84 ± 0.08 /day and 0.11 ± 0.011 /day, respectively, at an operating temperature of 60 °C. At temperatures above 60 °C, the specific methanol utilization coefficient and the specific growth coefficient declined sharply. Over 99% of the methanol was removed from the synthetic evaporator condensate at temperatures of 55 and 60 °C. The lower specific methanol utilization coefficients, observed at higher temperatures, resulted in lower methanol removal efficiencies at temperatures of 65 and 70 °C.

4. The mixed culture could be acclimatized directly at the optimal operating temperature of 60 °C following inoculation.

5. The decline in the specific methanol utilization coefficient and the specific growth coefficient, at an operating temperature above 60 °C, was not due to the rate at which

the temperature was increased. However, the rate at which the temperature was increased did have a significant effect on the instantaneous specific methanol utilization coefficient. Instantaneous temperature increases in the range of 5 °C resulted in an instantaneous decline in the specific methanol utilization coefficient. Instantaneous temperature increases of approximately 1 °C did not significantly affect the instantaneous specific methanol utilization coefficient.

6. A relatively simple model was proposed and used to accurately estimate the effect of temperature on methanol removal kinetics in an MBR over the range of temperatures investigated.

7. At increasing operating temperatures, a larger fraction of the methanol consumed was converted to energy (i.e. CO_2), reducing the observed growth yield.

The results indicated that the mixed microbial culture could be inoculated from one single source (activated sludge plant at a kraft pulp mill) and acclimatized directly at the optimal operating temperature of 60 °C. The operating temperature did have a significant effect on the biological removal of methanol from evaporator condensate. Based on the observed results and the model developed to estimate the effect of the operating temperature on methanol removal, the optimal operating temperature for the biological removal of methanol from evaporator condensate was estimated to be approximately 60 °C. Beyond an operating temperature of 60 °C, the specific methanol utilization coefficient declined sharply. Therefore, the operating temperature should be kept as high as possible, but less than or equal to 60 °C in the MBR. Some pre-cooling or provisions for cooling of the evaporator condensate in the design of the high temperature MBR may be required if the temperature of the evaporator condensate waste stream produces an operating temperature in excess of 60 °C in the MBR.

By using the proposed model, existing commonly-used simulation packages that model biological removal kinetics in wastewater treatment systems could be easily updated to account for the inactivating effect of elevated temperatures on microbial kinetics.

Effect of Evaporator Condensate Matrix on the Biological Removal of Methanol

The third experiment, presented in Chapter 6, investigated the effects of the contaminant matrix present in real evaporator condensate on the biological removal of methanol. The biological treatment system used in the third experiment was operated at the optimal operating temperature of 60 °C, as determined during the second experiment. The major conclusions from the experiment investigating the effects of the contaminant matrix present in real evaporator condensate are as follows.

1. Over 99% of the methanol contained in real evaporator condensate was removed during high temperature biological treatment. The methanol concentration of methanol in the evaporator condensate was reduced from approximately 964 ± 272 mg/L to below detection limits (approximately 0.5 mg/L).

2. The observed specific methanol utilization coefficient for the treatment of real evaporator condensate using an MBR was lower than that observed when treating synthetic evaporator condensate. However, the reduction in the specific methanol utilization coefficient was not a result of direct toxic response to the compounds present in the real evaporator condensate matrix. The reduction was due to a shift in the composition of the microbial community present in the MBR mixed liquor.

3. In the presence of both methanol and non-methanolic substrates, non-methylotrophic microorganisms compete with methylotrophic microorganisms for the available methanol. Partial-methylotrophic microorganisms exhibited a lower specific methanol utilization coefficient (0.29/day) than methylotrophic microorganisms (0.84/day). This resulted in an overall specific methanol utilization coefficient of 0.59 /day.

The specific methanol utilization coefficient observed when treating 100 % real evaporator condensate is more than 30 % higher than previously reported by others for biological systems treating evaporator condensate at much lower temperatures (Barton et

al., 1996). However, as observed in the third experiment, the composition of the evaporator condensate matrix can significantly affect the methanol removal kinetics. Therefore, it is not possible to confirm whether the lower observed specific methanol utilization coefficient reported by others at lower operating temperatures is due to the effect of the operating temperature, or to matrix effects associated with evaporator condensate that may have different characteristics. Nonetheless, the results confirm that it is possible to achieve relatively high methanol removal rates when operating a biological treatment system at an elevated temperature. The major benefit of operating at a high temperature is that no, or minimal, cooling of the evaporator condensate is required before treatment and that the heat content of the treated evaporator condensate can be recovered.

Considering that methanol removal is the main treatment objective, the results indicated that the evaporator condensate should be treated separately from other wastewater streams, in a kraft pulp mill, that would likely contain non-methanolic organic contaminants. Treatment of the segregated evaporator condensate could result in a higher specific methanol utilization coefficient than that which would be possible if the evaporator condensate were mixed with other process waste streams before treatment.

Removal of Non-Methanolic Contaminants from Evaporator Condensate During High Temperature Biological Treatment

The fourth experiment, presented in Chapter 7, investigated the removal of non-methanolic contaminants from real evaporator condensate during high temperature biological treatment. The major conclusions from the experiment investigating the removal of non-methanolic contaminants from evaporator condensate are as follows.

1. Approximately 93 % of the organic contaminants contained in the influent evaporator condensate, measured as TOC, can be removed during high temperature biological treatment. The concentration of TOC in the evaporator condensate was reduced from

504 ± 137 mg/L to 52 ± 3.6 mg/L. The biological removal of methanol accounted for approximately 78 % of the TOC removed. TOC removal due to stripping by the aeration system was not significant.

2. The residual TOC concentration in the MBR at the end of each batch feed cycle consisted of non-biodegradable compounds contained in the influent evaporator condensate and microbial products generated by the mixed culture in the MBR. The amount of non-biodegradable microbial products formed was estimated to be approximately 2 % of the influent organic content of the evaporator condensate, as TOC.

3. The residual TOC concentration in the MBR at the end of each batch feed cycle did not vary significantly, even though the influent TOC concentration varied significantly. The 90% confidence interval for the TOC concentration remaining in the MBR at the end of selected batch feed cycles was ± 3.6 mg/L. The 90 % confidence interval for the TOC concentration in the influent evaporator condensate was ± 137 mg/L.

4. TOC removal followed a pseudo-first order relationship. The specific TOC utilization coefficient was estimated to be 0.66 ± 0.056 /day. The results suggest that the initial TOC removal rate was higher than that for methanol. The initially high TOC removal rate is likely due to the rapid biological oxidation of easily biodegradable compounds contained in the condensate matrix.

5. Over 99% of the RSC were removed from the evaporator condensate using a high temperature MBR. The concentrations of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl sulphide, were reduced to below detection limits (approximately 0.4 mg/L), during high temperature biological treatment using an MBR. The results suggested that up to approximately 67 and 97 % of the influent methyl mercaptan and hydrogen sulphide, respectively, were abiotically oxidized in the MBR. The remaining fractions were stripped from the MBR due to the aeration

system. Dimethyl sulphide and dimethyl disulphide were completely removed from the evaporator condensate during treatment by stripping due to the aeration system.

These results indicated that in addition to methanol, non-methanolic contaminants present in real evaporator condensate can be effectively removed during high temperature biological treatment. Approximately 93 % of the organic contaminants, measured as TOC, contained in the influent condensate were removed during high temperature biological treatment using an MBR. The remaining organic contaminants were non-biodegradable. Relatively constant effluent TOC concentrations can be expected for a high temperature MBR treating evaporator condensate for reuse.

These results suggested that methyl mercaptan and hydrogen sulphide were rapidly oxidized in the mixed liquor contained in the high temperature MBR. To minimize the amount of these RSC that are stripped to the atmosphere due to the aeration system and to maximize the amount that is oxidized, the head-space in the MBR could be recycled back into the mixed liquor. This could increase the amount of these RSC that are abiotically oxidized. However, further research is required to determine the optimal operating parameters to maximize the abiotic oxidation of methyl mercaptan and hydrogen sulphide in a high temperature MBR treating evaporator condensate.

As an alternative, the RSC contained in the off-gas from a high temperature biological treatment system could be oxidized using a designated catalytic incinerator or a biofilter. The off-gas could also be hard-piped to an existing power or recovery boiler for incineration. The incineration of RSC in the power or recovery boiler could also potentially reduce the overall dioxin emissions from a kraft pulp mill (Uloth, 1999).

Conceptual Design and Cost Estimates for a Full-Scale High Temperatue MBR for the Treatment of Evaporator Condensate for Reuse

In the final part of the study, presented in Chapter 8, a conceptual design was developed for a full-scale high temperature MBR for the treatment of evaporator condensate for

reuse and capital and operating costs were estimated. The cost estimates for a high temperature MBR were compared to the cost estimates for a steam stripping system. Steam stripping is considered by some as the most attractive conventional technology for the treatment of evaporator condensate for reuse. The major conclusions from the conceptual design and cost estimate are as follows.

1. Based on the kinetic information collected during experiments 1 to 4, it was possible to develop a conceptual design for a full-scale high temperature MBR for the treatment of evaporator condensate, from a local kraft pulp mill, for reuse.

2. The combined capital and operating costs for a high temperature MBR were estimated to be substantially less than those for a steam stripping system.

3. An MBR is capable of achieving a higher contaminant removal efficiency than a steam stripping system.

The results from the laboratory experiments indicated that high temperature biological treatment of evaporator condensate for reuse is technically feasible. The results from the conceptual design and cost estimate indicates that in addition to being technically feasible, high temperature biological treatment is also more effective and more economically attractive than steam stripping for the treatment of evaporator condensate for reuse.

9.2 Recommendations for Further Studies

The results from the present study have improved our understanding of the physical, chemical and biological processes that occur during the high temperature biological treatment of evaporator condensate using an MBR. The results provided the knowledge necessary to perform a conceptual design for a high temperature MBR for the treatment of evaporator condensate for reuse. As with many research projects, a number of new

questions were generated. Some of the most crucial to our full understanding of a high temperature biological treatment of evaporator condensate using a high temperature MBR are as follows.

1. What are the effects of temperature variations, caused by transient loads or plant shutdowns, on the biological treatment of evaporator condensate for reuse. The effect of temperature variations was investigated when the operating temperature was increased as presented in Chapter 5. However, the effect of the magnitude and duration of the temperature variations was not investigated.

2. Although the cross-flow velocity through the membrane component of the MBR was kept constant during all experiments, preliminary results from a parallel study indicated that the shear produced in the recycling line of an MBR can impact contaminant removal kinetics (Ronteltap, 1999). The effects caused by the shear are of concern when selecting the recycling rate through the membrane component of the MBR and also when adapting pilot scale results to a full-scale system. Further research on the effect of shear produced in the recycling line on the activity of microbial populations in an MBR are required to properly select the recycling rate and scale-up factors.

3. As presented in Chapter 5, the observed growth yield decreased as the operating temperature increased over the range of temperatures investigated (55 to 70 °C). However, it is not clear if the decline in the observed growth yield is due to a reduction in the true growth yield or to an increase in the decay rate. Further research is required to confirm the mechanism responsible for the decline in the observed growth yield.

4. As suggested by the results presented in Chapter 7, hydrogen sulphide and methyl mercaptan are removed from the evaporator condensate, during treatment using a high temperature MBR, by abiotic oxidation. A better understanding of the kinetics

and fate of these RSC during abiotic oxidation is required to properly operate a high temperature MBR for the removal of hydrogen sulphide and methyl mercaptan.

5. A few studies have investigated the effect of reusing evaporator condensate as process water (Section 2.2.2). A parallel preliminary study investigating the reuse of biologically treated evaporator condensate that was subsequently filtered using an ultrafiltration membrane was done. However, these preliminary results are not conclusive (personal communication, Duff S., 1999, Department of Chemical Engineering, University of British Columbia, Vancouver, Canada). Further research is required to confirm that evaporator condensate treated using a high temperature MBR are sufficiently clean to be reused as process water.

6. Nutrients were added in excess during the present study. Further research is required to determine the nutrient requirements for treating evaporator condensate using a high temperature MBR. Optimizing the nutrient requirements is necessary to determine the exact chemical costs to treat evaporator condensate for reuse.

By addressing these questions it would be possible to further increase our understanding of the physical, chemical and biological processes that occur during the high temperature biological treatment of evaporator condensate using an MBR.

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Appendix 1 – Analytical Methods, Experimental Procedures and Off-Line Tests

A1.1 Analytical Methods

The analytical methods used are presented below.

Conductivity

The conductivity was measured using a Radiometer Copenhagen CDM3 conductivity meter. The samples were acclimatized to a standard temperature of 20 °C before measurement.

Dissolved Oxygen Concentration

The dissolved oxygen concentration was measured using an Oxyguard Type I (Point Four Systems Inc., Vancouver, Canada) portable dissolved oxygen probe. The dissolved oxygen meter was calibrated based on the saturation concentration for oxygen in water at the temperature of the solution being investigated.

Methanol Concentration

The concentration of methanol was measured by direct injection of filtered (0.45 μm cellulose nitrate syringe membrane filter) aqueous samples into a gas chromatograph (HP5890, Hewlett Packard Co., Avondale, PA, USA) with a 30 m long wide bore capillary column (DBWAX 0.53 MMID, J & W Scientific, Folsom, CA, USA) and a flame ionization detector.

pH

The pH was measured using a Beckman Model PHI 44 pH meter.

Reduced Sulphur Compounds (RSC) Concentration

An analytical method was developed to measure the concentration of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide in aqueous samples (Bérubé et al., 1999). The concentration of the individual RSC was measured by direct injection of filtered (Glass microfibre filters, Whatman 934-AH; Whatman International Ltd., Maidstone, England) aqueous samples into a gas chromatograph (HP5890, Hewlett Packard Co., Avondale, PA, USA) with a 30 m long wide bore capillary column (DBWAX 0.53 MMID, J & W Scientific, Folsom, CA, USA) and a flame photometric detector (HP5890A option 240, Hewlett Packard Co.). A re-print of the method is presented in section A1.3.

Total Organic Carbon Concentration

The concentration of total organic carbon (TOC) was measured by combustion-infrared method using a TOC analyzer (Shimadzu TOC-500, Columbia, USA) according to Standard Methods (APHA/AWWA/WEF, 1995). The inorganic component of the sample was removed by acidifying and subsequently purging the inorganic carbon from the sample by stripping it out as CO_2 by bubbling oxygen through the sample. Filtered TOC samples were filtered through a 0.45 μm cellulose nitrate syringe membrane filter cartridge before analysis.

Total and Volatile Suspended Solids (TSS and VSS) Concentration

The concentration of total and volatile suspended solids was determined according to Standard Methods (APHA/AWWA/WEF, 1995).

A1.2 Experimental Procedures

The experimental procedures developed during the present study are presented below.

Biomass Inactivation

As presented in experiments 1 through 4 (Chapters 4 to 7), sodium azide was used to inactivate the biomass. Tests were done using inactivated biomass to investigate the abiotic contribution to the contaminant removal rates measured during high temperature biological treatment. Liver (1990) reported that sodium azide could be used to effectively inactivate biomass in an aerobic biological treatment system. Therefore an off-line experimental procedure was developed, as presented below, to determine the amount of sodium azide required to inactivate the biomass.

The off-line batch methanol removal tests were completed using 100 mL aliquots of mixed liquor collected from the MBR during the feasibility study (Chapter 4). The mixed liquor was collected from the MBR approximately 5 minutes following the start of selected batch feed cycles. The mixed liquor aliquot was then immediately transferred into a 250 mL flask and incubated at 55 °C in a stirred water-bath. Air was added through a fine bubble stone diffuser to ensure non-limiting dissolved oxygen conditions. The minimum measured dissolved oxygen concentration in the aerated mixed liquor was approximately 3.5 mg/L. Sodium azide was added to the flask and the rate of methanol removal was determined by measuring the change in the concentration of methanol in the flask at 10, 25, 40 and 50 minutes following the start of the incubation period. This was repeated with different amounts of sodium azide added to the flasks.

Figure A1-1 illustrates the relationship between the concentrations of sodium azide in the flask and the zero order coefficient for the removal of methanol. As discussed in Chapters 4 to 6, methanol removal followed a zero order rate. The zero order coefficient for the removal of methanol decreased rapidly when sodium azide was added. At a sodium azide concentration above 0.5 %, there was no further significant decrease in the

zero order coefficient for the removal of methanol. The residual rate of methanol removal at a sodium azide concentration greater than 0.5 % was attributed to the stripping of methanol to the atmosphere due to the air added through the fine bubble stone diffuser (see Figure A1-1).

A sodium azide concentration of 1 % was selected to ensure the complete inactivation of the biomass.

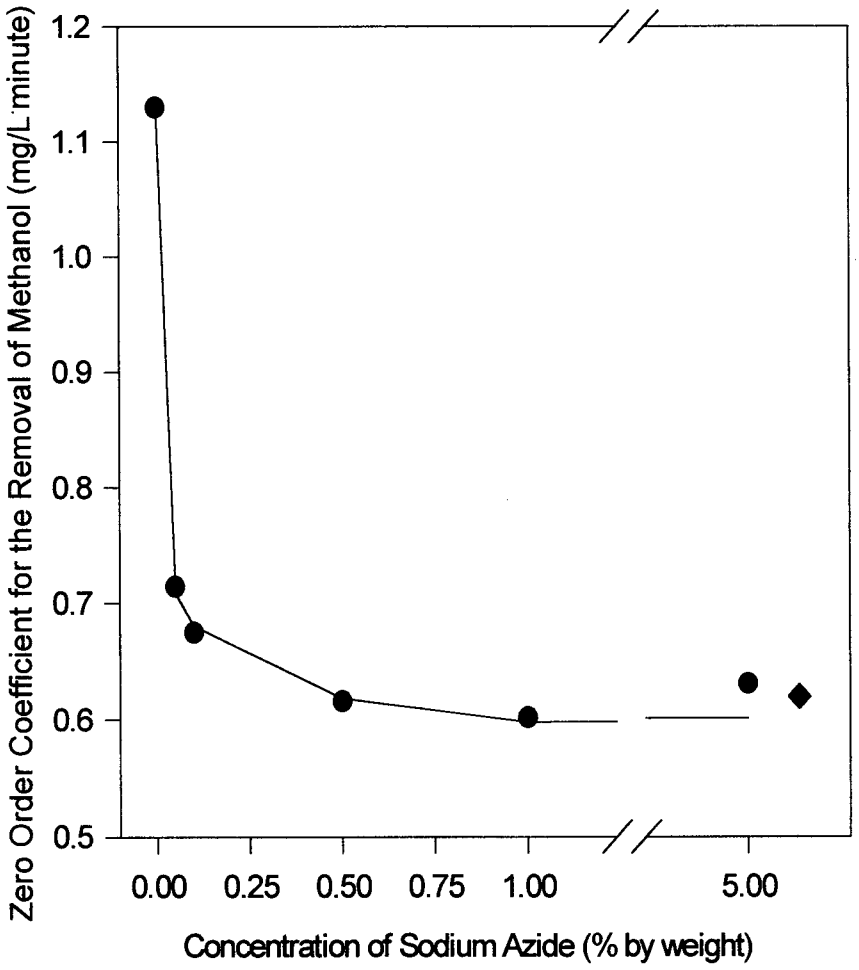

Figure A1-1 Effect of Sodium Azide on Zero Order Coefficient for the Removal of Methanol

(● - biomass with sodium azide; ◆ - Clean water stripping test)

Non-Limiting Dissolved Oxygen Conditions

The required aeration rate to provide non-limiting dissolved oxygen conditions in the MBR was determined by investigating the rate of methanol removal in the MBR for different aeration rates.

As discussed in Chapters 4 to 6, methanol removal followed a zero order rate. Figure A1-2 illustrates the relationship between the zero order biological methanol removal coefficient and the aeration rate for the primary MBR used during the feasibility study. The zero order coefficient for the biological removal of methanol increased as the aeration rate increased up to an aeration rate of approximately 1.6 L/minute. Above 1.6 L/minute, the methanol removal coefficient was relatively constant. To verify that sufficient oxygen was being added, the aeration to the MBR was modified to utilize a 50% air and a 50 % oxygen mixture, by volume, at a rate of 1.6 L/minute. A relatively similar zero order coefficient for the biological removal of methanol was observed when a 50-50 mixture of air and oxygen was used. For comparison, 100 % oxygen was also added to the MBR at a flow rate of 0.33 L/minute. This oxygenation rate was equivalent to aerating with air at a rate of 1.6 L/minute. Again, a relatively similar methanol removal coefficient was observed. Based on these results, an aeration rate of 1.6 L/minute was selected to prevent excessive stripping of the volatile contaminants contained in the evaporator condensate and to provide non-limiting dissolved oxygen conditions.

Aerating at a rate of 1.6 L/minute resulted in a minimum dissolved oxygen concentration of approximately 2 mg/L in the MBR during each batch feed cycle. The dissolved oxygen concentration in the MBR could not be continuously monitored due to the instability of the available dissolved oxygen probe at elevated temperatures.

The required aeration rate was determined similarly for the small MBR. For the small MBR, an aeration rate of 0.5 L/minute provided non-limiting dissolved oxygen conditions.

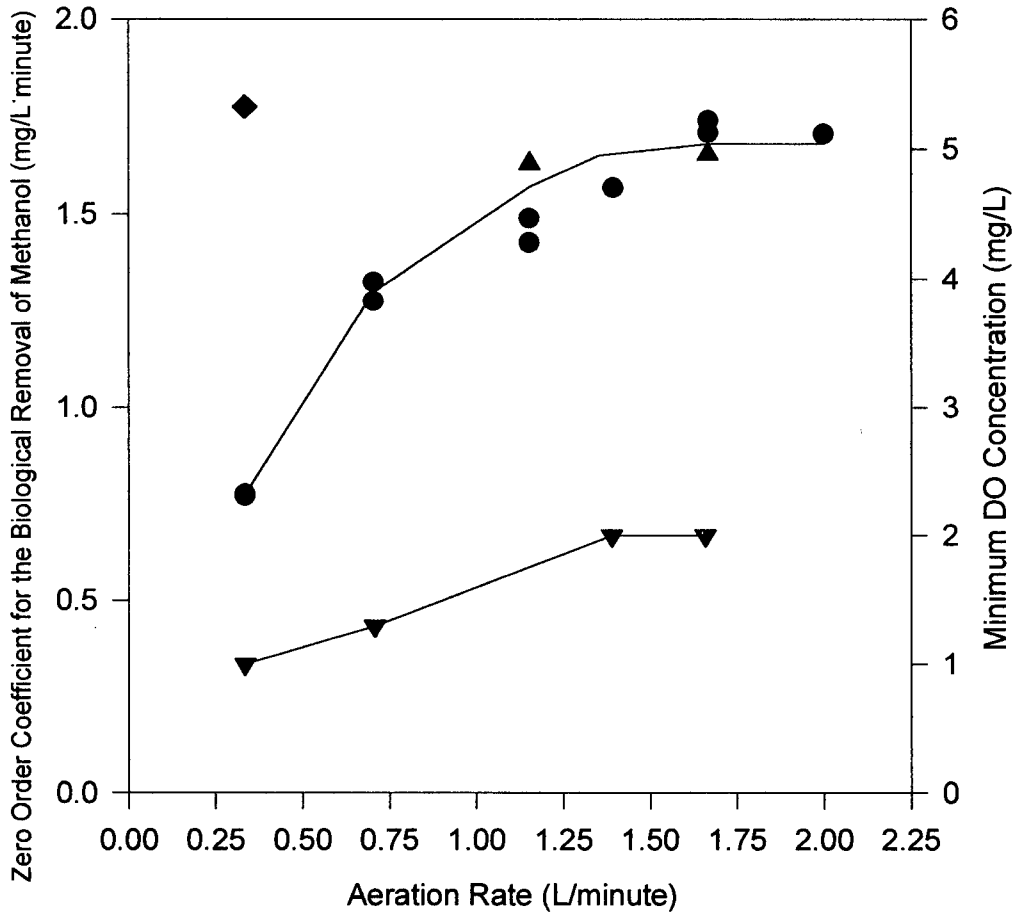

Figure A1-2 Effect of Aeration Rate on Zero Order Coefficient for the Biological Removal of Methanol

(● - 100 % air; ◆-100 % oxygen; ▲ - 50 % air, 50 % oxygen;

minimum dissolved oxygen concentration:▼)

When operating parameters such as temperature, pH or feed composition were varied, non-limiting dissolved oxygen conditions were verified by comparing the zero order coefficient for the biological removal of methanol when the aeration to the MBR consisted of air only and when a 50-50 mixture of air and oxygen was used. Non-limiting dissolved oxygen conditions were assumed to prevail if the zero order coefficient for the biological removal of methanol was the same for both aeration scenarios.

For all experiments, an aeration rate of 1.6 L/minute provided non-limiting dissolved oxygen conditions in the primary and secondary MBR regardless of the operating temperature. This is consistent with results from Vogelaar et al. (2000) who observed that the combined effect of an increase in the oxygen transfer coefficient and a decrease in the oxygen saturation concentration with an increase in temperature resulted in a constant oxygen transfer rate regardless of the operating temperature. An aeration rate of 0.5 L/minute provided non-limiting dissolved oxygen conditions in the small MBR.

Observed Growth Yield

The observed growth yield was determined using the ratio of the cumulative mass of microorganisms removed from the MBR, including any change in the total mass of microorganisms in the MBR, to the cumulative mass of methanol consumed, measured during the steady state monitoring period for the different experiments.

Qualitative Bacterial Examination

The mixed microbial community present in the MBR was qualitatively examined using acridine orange staining and a fluorescent microscope. Under a fluorescent light, live microorganisms that have been stained with acridine orange are bright orange and non-living material is translucid (Francisco et al., 1973).

One drop of a mixed liquor aliquot obtained from the MBR reactor tank was diluted 10 times with distilled water and placed on a glass slide and then heat fixed by passing the slide over a bunsen burner several times until the drop was dried. Several drops of 0.003% acridine orange solution were then added onto the fixed sample. After approximately 5 minutes, the acridine orange solution was rinsed off the slide with a gentle stream of distilled water and a cover slip was applied. An epifluorescence microscope (Zeiss 2Fl-46 63 00-9900) with a 40 x magnification was then used to observe the stained microorganisms present on the slide.

Photographs were periodically taken of the stained microorganisms using a Nikon M35s, 35 mm camera with a microscope adaptor (Nikon AFM-86030).

A1.3 Off-Line Batch Testing Apparatus

A1.3.1 Identification of Direct Toxic Effects

Off-line batch treatability tests were done to investigate potential direct toxic effects of the contaminants present in the real condensate matrix. The off-line, batch treatability tests were completed using 100 mL aliquots of mixed liquor taken from an MBR during growth on 100 % synthetic evaporator condensate, at 60 °C. The aliquots were collected at the end of selected batch feed cycles (at t = 175 minutes). The mixed liquor aliquots were placed in 200 mL glass flasks, feed and nutrients were added, and the mixtures were incubated at a temperature of 60 °C and mixed at a rotational speed of 60 rpm in an incubator-shaker (Inova 4230 incubator/shaker). The temperature of the flasks, feed and nutrients was adjusted to 60 °C before the start of the test. The rates of methanol removal were monitored by measuring the changes in the concentration of methanol in the flasks over a 65 minute incubation period. Samples were collected 5, 20, 35, 50 and 65 minutes following the start of the incubation period. In various batch tests, the amount of real evaporator condensate in the feed was set at 0 %, 10 %, 60 % or 100 %, based on the mass of methanol. Additional batch tests were completed with a 100 % real evaporator condensate feed, but with the suspended solids concentration increased 10-fold. This was done to determine whether contaminants associated with particulate material in the real condensate could have been a source of toxicity. The concentration of suspended solids in the real evaporator condensate was increased by allowing the solids to settle from solution and subsequently decanting and discarding the supernatant.

Tests using inactivated biomass were used to investigate the abiotic removal of methanol under batch conditions. The biomass was inactivated by adding sodium azide to obtain a 1% concentration in the flasks (see Appendix 1).

A1.3.2 Radio-Tracing Tests

The effect of non-methanolic compounds present in a real evaporator condensate matrix on the composition of the microbial community present in the MBR was investigated using off-line batch radio-tracing tests. Off-line batch degradation tests using radio-labeled methanol were completed using 1 mL aliquots of mixed liquor taken from the MBR. The mixed liquor was immediately transferred into a 15 mL hypo-vial and capped with a silicone septum. The mixed liquor was collected ten minutes following the start of selected MBR feed events. A 10 µl volume of C^{14}-labeled methanol (4 µCi/ml – IMC Biochemicals) was then injected into the hypo-vial. The hypo-vial was then incubated at 60 °C for 120 minutes. For all conditions examined, the measured concentration of methanol in the mixed liquor was reduced to less than 0.5 mg/l (method detection limit) during the incubation period. The temperature of all vials and caps was adjusted to 60 °C before the start of the test. After 60 minutes of incubation, 0.5 mL of caustic solution (0.5 M NaOH) was injected directly into a 2 mL GC-vial contained inside the 15 mL hypo-vial, to adsorb the CO_2 produced from the complete oxidation of methanol. After the 120 minute incubation period, 0.5 mL of acid solution (12 M HCl) was added to the mixed liquor aliquot to stop biological activity and to volatilize any remaining CO_2 from the mixed liquor. The 15 mL hypo-vial was then gently shaken for 15 minutes. The caustic solution was collected and transferred to a scintillation counting vial and mixed with 5 mL of scintillation cocktail (Scintiverse II, Fisher Scientific). The mixed liquor aliquot was filtered through a 0.45 µm cellulose acetate membrane and rinsed with distilled water. The membrane was then inserted into a scintillation vial, the biomass was lysed by adding 1 mL of Scintigest (Fisher Scientific) and 5 mL of scintillation cocktail (Scintiverse II) was then added. The amount of radio-labeled methanol as biomass (membrane samples) and as CO_2 (NaOH samples) was measured using a scintillation counter (Beckman LS6500). Blanks containing mixed liquor with inactivated biomass indicated that abiotic adsorption of radio-labeled carbon onto the biomass was negligible. The biomass was inactivated by adding sodium azide to obtain a 1% concentration in the mixed liquor aliquot (see Appendix 1).

A1.4 Off-Gas Traps for the RSC Mass Balance

To determine the fate of RSC during high temperature treatment using an MBR, a mass balance was done on the MBR by monitoring all influent, effluent and residual RSC concentrations during selected batch feed cycles.

The concentration of RSC in the influent was determined by sampling and analyzing the influent evaporator condensate, from the pre-heating tank outflow line, before introducing the evaporator condensate into the MBR for selected feed cycles. Immediately following the addition of the evaporator condensate, the influent and effluent lines to the MBR were closed and the reactor cover was sealed shut. This resulted in a fully closed system for which the only input was from the aeration system and the only output was the off-gas from the MBR.

The off-gas was hard piped through three traps (50 mL airtight glass beakers) arranged in series, as illustrated in Figure A1.1, to capture the RSC it contained. The first trap captured any foam or liquid that periodically escaped the MBR along with the off-gas. The second trap contained a caustic solution. The off-gas was bubbled through the caustic solution to captured the hydrogen sulphide and methyl mercaptan contained in the off-gas. Gaseous hydrogen sulphide and methyl mercaptan can be solubilized in an aqueous caustic solution as sulphide and mercaptan ions (Weast, 1986). The caustic trap contained 25 mL of 0.1 M NaOH solution in distilled and deionized water. A similar trap has been recommended by others to capture gases in an ionic form in aqueous solutions (Workers Compensation Board, 1984). The third trap contained ethanol. The off-gas was bubbled through ethanol to captured the dimethyl sulphide and dimethyl disulphide contained in the off-gas. Dimethyl sulphide and dimethyl sulphide are highly soluble in ethanol (Weast, 1986). The ethanol trap contained 25 mL of ethanol. As presented in Appendix 7, the ethanol trap also captured some residual methyl mercaptan that was not captured by the caustic trap. Methyl mercaptan is also highly soluble in ethanol (Weast, 1986). The off-gas from the MBR was piped through the RSC traps for the 60 minute period immediately following the start of selected batch feed cycles. To minimize the

re-volatilization of the captured RSC, the traps were removed and replaced at 5, 15, 30 and 45 minutes following the start of the selected batch feed cycles for the caustic traps and at 20 and 40 minutes following the start of the selected batch feed cycle for the ethanol traps. Replacing the traps significantly increased the capture efficiency. The caustic and ethanol traps were removed at different intervals to allow sufficient time to sample and replace the traps. The liquid contained in the removed traps was then sampled and analyzed for RSC. At the end of the 60 minute period, the liquid contained in the remaining traps was also sampled and analyzed for the RSC.

All RSC analyses were performed within approximately 10 minutes following sample collection. This was done to minimize the potential abiotic degradation of hydrogen sulphide and methyl mercaptan in the collected samples (Chen and Morris, 1972; Wilmot et al., 1988; Saunders, 1995).

The residual concentration of RSC in the MBR at the end of the 60 minute period was determined by sampling and analyzing the contents of the MBR for RSC at 60 minutes following the start of the selected feed cycles. All influent and effluent lines were then re-opened to resume normal MBR operation.

For two of the selected feed cycles, synthetic evaporator condensate was used as feed. The results from the mass-balance using synthetic evaporator condensate were compared to the results from the mass balance using real condensate to investigate the potential formation of degradation products from methyl mercaptan. Saunders (1995) observed that aqueous methyl mercaptan, in the presence of oxygen, can oxidize to dimethyl disulphide.

Tests using inactivated biomass were used to investigate the abiotic removal of RSC in the MBR. The biomass was inactivated by adding sodium azide to obtain a 1% concentration in the MBR (see Appendix 1).

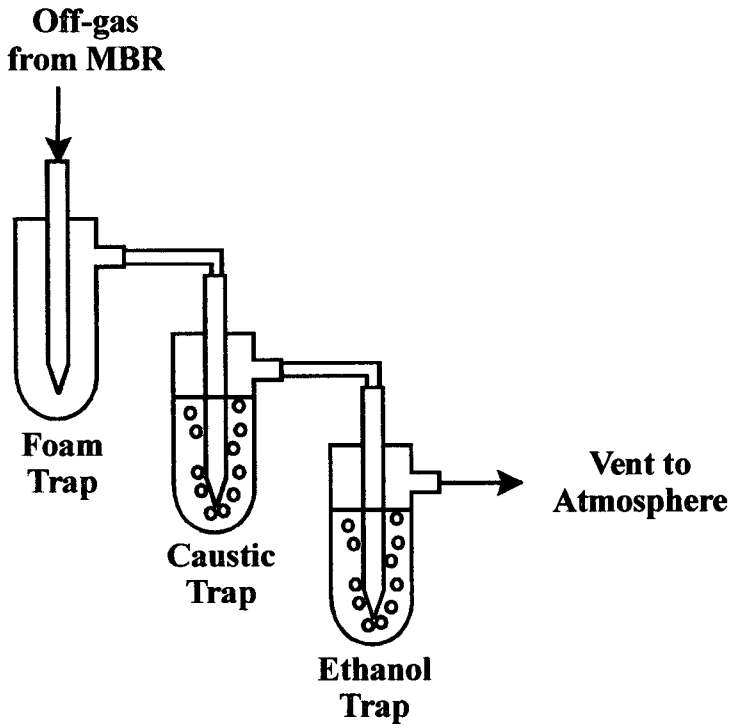

Figure A1.1 – Schematic of RSC Traps

The efficiency of the traps at capturing the RSC was determined by bubbling helium through a 50 mL airtight beaker, similar to those used for the RSC traps, which contained a 25 mL solution of RSC in distilled water. The off-gas from the beaker was captured and piped to the RSC traps. The capture efficiency of the traps was calculated by measuring how much of the RSC that were stripped from the solution were captured in the traps. Helium was used instead of air to estimate the capture efficiency to minimize abiotic oxidation of the RSC. As discussed in Section 7.4, aqueous hydrogen sulphide and methyl mercaptan can rapidly abiotically oxidize in the presence of oxygen. Helium was bubbled through the RSC solution at a rate of 25 mL/minute, which is volumetrically equivalent to the rate at which air was added to the MBR during the mass balance test.

The capture efficiency was investigated using three different RSC solutions. The RSC solutions contained hydrogen sulphide, methyl mercaptan or a mixture of dimethyl sulphide and dimethyl disulphide. The recovery tests were done over a 20-minute period for the solutions containing hydrogen sulphide or methyl mercaptan. The concentration

of hydrogen sulphide, or methyl mercaptan, in the solution was measured at the start and at the end of the 20-minute capture test. The concentration of hydrogen sulphide, or methyl mercaptan, in the traps was measured at the end of the 20-minute capture test. For the solutions containing dimethyl sulphide and dimethyl disulphide, the capture test was done over a 40-minute period to account for the lower volatility of these RSC. The concentrations of dimethyl sulphide and dimethyl disulphide in the RSC solution was measured at the start and at the end of the 40-minute capture test. To minimize the revolatilization of the captured dimethyl sulphide and dimethyl disulphide, the traps were removed and replaced 20 minutes following the start of the capture test. The concentration of dimethyl sulphide and dimethyl disulphide in the traps collected 20 and 40 minutes following the start of the capture test was measured. The results are presented in Tables A1.1 to A1.2. As presented, the capture tests were done in duplicate.

Table A1.1 – Capture Efficiency of RSC Traps for Hydrogen Sulphide and Methyl Mercaptan

	Hydrogen Sulphide		Methyl Mercaptan	
	3-Jan-00		3-Jan-00	
	Test 1	Test 2	Test 1	Test 2
Solution t=0 (mg)	0.14	0.15	0.18	0.19
t= 20 min Caustic (mg)	0.01	0.00	0.12	0.12
t=20 min Ethanol (mg)	0.00	0.00	0.02	0.03
Solution t=20 (mg)	0.00	0.00	0.02	0.02
Recovered (mg)	0.01	0.00	0.13	0.15
Removed (mg)	0.14	0.15	0.16	0.16
Percent Captured (%)	9.1	0.0	82.8	89.2
Average Capture (%)	4.5		86.0	

(samples collected from solution vial and RSC traps at times indicated)

Table A1.2 – Capture Efficiency of RSC Traps for Dimethyl Sulphide and Dimethyl Disulphide

	Test 1		Test 2	
	3-Jan-00		4-Jan-00	
	DMS	DMDS	DMS	DNDS
Solution t=0 (mg)	0.14	0.24	0.14	0.23
t= 20 min Caustic (mg)	0.02	0.02	0.02	0.01
t= 40 min Caustic (mg)	0.00	0.00	0.00	0.00
t=20 min Ethanol (mg)	0.03	0.08	0.04	0.08
t=40 min Ethanol (mg)	0.03	0.05	0.03	0.06
Solution t=40 (mg)	0.03	0.06	0.02	0.05
Recovered (mg)	0.08	0.15	0.08	0.15
Removed (mg)	0.11	0.18	0.11	0.18
Percent Capture (%)	72.1	87.1	71.1	81.9
Average Capture (%)	71.6	84.5		

(samples collected from solution vial and RSC traps at times indicated)

The ability of the traps to capture methyl mercaptan, dimethyl sulphide and dimethyl disulphide was relatively good. The capture efficiencies for methyl mercaptan, dimethyl sulphide and dimethyl disulphide were 86, 72 and 84 %, respectively. The non-complete recovery of these RSC was attributed to the mass transfer limitations of these RSC from the gaseous phase (off-gas) to the liquid phase (caustic and ethanol traps) and to the revolatilization of the captured RSC. No dimethyl disulphide was detected in the traps when investigating the capture efficiency for methyl mercaptan. This indicates that methyl mercaptan was not abiotically oxidized to dimethyl disulphide as was observed in the MBR (see Section 7.4).

A negligible amount of the hydrogen sulphide removed from the RSC solution was captured in the traps (less than 5 %). However, there was no odor associated with the off-gas that was vented to the atmosphere down-stream of the traps. This suggests that the vented off-gas did not contain any hydrogen sulphide. Therefore, the hydrogen sulphide was converted to other sulphur compounds either in the RSC solution or in the traps. As discussed in Section 7.4, aqueous hydrogen sulphide can oxidize very rapidly in the presence of oxygen. Although helium was used during the capture tests, some

oxygen was present in the distilled water used to make-up the RSC solution and the caustic trap. Consequently, the RSC traps were not considered to adequately capture hydrogen sulphide. Further studies are required to determine the fate of hydrogen sulphide during the capture test.

A1.5 Measurement of Reduced Sulphur Compounds Contained in Aqueous Matrices by Direct Injection into a Gas Chromatograph with a Flame Photometric Detector (Re-print of Bérubé et al., 1999)

Abstract

An analytical method was developed to measure the concentration of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide contained in aqueous matrices (distilled water, tap water, kraft mill condensates and membrane bioreactor mixed liquor) by direct injection of aqueous samples into a gas chromatograph with a flame photometric detector (GC-FPD). The analytical method requires a small sample volume (2 ml), sample preparation and analysis can be completed within 20 minutes and no complex sampling apparatus is needed. Consistent results and good recoveries were observed in all matrices investigated over the range of concentrations examined. The relationship between the normalized peak area obtained from the GC-FPD and the concentration of the RSCs examined did not follow the theoretical power law exponent of two. The power law exponent appeared to decrease with the organic fraction associated with each RSC. The observed power law exponents for hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide were 1.92, 1.90, 1.66 and 1.72, respectively.

Introduction

A study was conducted to investigate the removal of reduced sulphur compounds (RSCs) from kraft pulp and paper mill condensates using a high temperature membrane bioreactor (MBR). The performance of the MBR was monitored by measuring the batch biotic and abiotic removal rates for the RSCs (hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide) in the MBR. The rates were determined by withdrawing samples from the MBR and measuring the rate of change in the concentration of RSCs.

A gas chromatograph with a flame photometric detector (GC-FPD) is commonly used to measure the concentration of RSCs in aqueous samples (Peppard, 1988; Sola et al., 1997; Richards et al., 1994; Saunders, 1995). However, the injection of aqueous samples directly into a GC-FPD is not recommended because it can cause a number of problems. Primary, the injected water can extinguish the detector flame and non-volatile material contained in the aqueous sample can coat the GC injection port and column. To avoid these problems, most analytical methods specify that the volatile compounds be separated from an aqueous sample before analysis by either purge and trap techniques or head-space gas sampling (Peppard, 1988; Sola et al., 1997; Richards et al., 1994; Saunders, 1995; Werkhoff and Bretschneider, 1987; Caron and Kramer, 1989; Sullivan et al., 1995). There are a number of disadvantages associated with purge and trap techniques when applied to the measurement of RSCs in aqueous matrices. First, a relatively complex and expensive purging and trapping apparatus is required (Sola et al., 1997; Richards et al., 1994; Saunders, 1995; Werkhoff and Bretschneider, 1987; Caron and Kramer, 1989). In addition, gaseous sulphides strongly adsorb to glass potentially leading to poor recoveries if the glassware used for purging and trapping the volatile RSCs is not properly cleaned and "deactivated" (Caron and Kramer, 1989). Second, it is often difficult to ensure that 100 % of a compound with low volatility has been entirely purged again potentially leading to poor recoveries (Saunders, 1995). Third, it can take a number of hours to complete the purge and trap steps (Saunders, 1995). Some RSCs such as hydrogen sulphide and methyl mercaptan are relatively unstable (Saunders, 1995; Chen and Morris, 1978). Consequently, the characteristics of the sample can change during sample storage and analysis. Finally, a relatively large volume of sample, up to 100 ml, is required by purge and trap techniques (Caron and Kramer, 1989). This is of major disadvantage when many samples are to be withdrawn from a laboratory or bench scale system within a short period of time, to assess the kinetics associated with the removal of RSCs. The main disadvantage associated with the injection of the head-space gas from a sample vial directly into a GC is that the relationships between the concentrations of volatile RSCs in the head-space and those of the aqueous sample (Henry's Law) are highly influenced by the temperature of the sample (Sullivan et al., 1995; Blackwell et al., 1979). Therefore, all samples must be analyzed at precisely the

same temperature, requiring a constant temperature automatic sampler which can significantly add to the complexity and cost of the analytical apparatus. Also, equilibrium conditions must be assumed between the vapor phase and the aqueous phase for all compounds of interest.

An analytical method which consists of direct injection of an aqueous sample into a GC-FPD was developed to address the inadequacies of the above techniques. The analytical method measures the concentration of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide in aqueous matrices which consists of either distilled water, tap water, kraft pulp mill condensates or mixed liquor from an MBR.

Experimental

Sample Preparation

The samples were prepared before analysis to remove particulate material. Approximately 2 ml of sample was collected with a 10 ml glass syringe and filtered through a 25 mm syringe filter holder (Gelman Sciences, Ann Arbor, MI, USA). Several filtering materials were investigated. Cellulose nitrate, cellulose acetate, nylon and paper filters all resulted in recoveries less than 75 %. Glass microfibre filters (Whatman 934-AH; Whatman International Ltd., Maidstone, England) resulted in satisfactory recoveries (see Results and Discussion Section).

For the analysis, 0.5 ml of filtered sample was introduced into a 2 ml GC vial. A 10 µl aliquot of thioanisole (99 % pure, Aldrich Chemicals Co., Milwaukee, USA) solution, consisting of 25 µl thioanisole in 100 ml methanol (99 % pure, Fisher Scientific, Fair Lawn, USA), was added to each GC vial to normalize the peak area for the RSCs (see Section 2.3). Thioanisole was selected because it was stable for an extended period of time and because the peak for thioanisole did not overlap with the peaks associated with the RSCs examined.

Gas Chromatography

A gas chromatograph (HP5890-II with a HP3396 Series II Intergrator; Hewlett Packard Co., Avondale, USA) with a flame photometric detector (HP5890A Option 240; Hewlett Packard Co.) was used to measure the concentrations of RSCs. Although initially the detector flame was periodically extinguished by the injected water, an increase in the detector temperature to 250 °C prevented the detector flame from being extinguished. Higher detector temperatures were not useful, because beyond 250°C, the baseline signal became highly variable.

A 1 µl volume of filtered sample was injected into the GC-FPD with a split ratio of 10:1. The slow injection speed setting for the automatic sampler (HP 7673 GC/SFC Automatic Injector, Hewlett Packard Co.) was used. Split injection reduced the quantity of non volatile material entering the column, reducing the chance of column blockage and/or ghost peaks. Perhaps most important, split injection reduced the amount of water entering the column and thereby, reduced the chances of extinguishing the detector flame. A wide bore capillary chromatography column (DBWAX 0.53 mmID, 30 m long, 1µm film thickmess; J & W Scientific, Folsom, CA, USA) was used. Helium (99.996 % pure, Praxair, Mississauga, Canada; with Supelco 23800 Carrier Gas Purifier, Supelco Inc., Bellefonte, USA) was used and the carrier gas at a flow rate of 5.8 ml/min.

The oven temperature program used to separate the individual RSCs was 40 °C for 5 minutes, followed by a temperature increase of 30 °C /min to an intermediate temperature of 160 °C, which was held for 3 minutes and finally a temperature increase of 40 °C /min to 200 °C. The hydrogen sulphide (1.16 min), methyl mercaptan (1.39 min) and dimethyl sulphide (1.66 min) peaks eluted at the initial temperature setting. The dimethyl disulphide (6.74 min) peak eluted during the transition to the intermediate temperature. The thioanisole (11.35 min) peak eluted at the intermediate temperature setting. The final temperature increase to 200 °C was done to purge any remaining volatiles from the column.

The GC-FPD was "conditioned" before and after every sample series by increasing the temperatures of the injection port, the oven and the detector to 20°C above their maximum analytical temperature (i.e. 180°C for injector port, 220°C for oven and 270°C for detector) for approximately two hours. Approximately 12 to 15 samples were analyzed per series. Since non-volatile material would remain in the sample following filtration, portions of such material could accumulate in the injection port and the column, potentially resulting in ghost peaks or plugging of the column. The injection port was cleaned approximately once per 4 to 5 sample series to remove accumulated non-volatile material by cleaning and deactivating the injector port glass insert as recommended by Caron and Cramer (1989), cleaning the injector port with a cotton swab soaked in methanol and replacing the injector port o-ring and septum.

Calibration

A calibration curve was constructed using a standard mixture of RSCs prepared by injecting 200 µl of hydrogen sulphide (98.5 % pure, Praxair) and 200 µl of methyl mercaptan (99.5 % pure, Aldrich Chemicals Co.) gas , at room temperature and atmospheric pressure, into a 58 ml capped glass vial filled with distilled water. A 15 µl mixture of 30 µl of dimethyl sulphide (98 % pure, Aldrich Chemicals Co.) and 30 µl of dimethyl disulphide (99 % pure, Aldrich Chemical Co.) in 2 ml of methanol was then injected into the 58 ml capped glass vial. All volumes were measured using a gas tight syringe. The vial was then shaken for 30 minutes to allow the RSCs to fully dissolve. All glass vials were cleaned and deactivated prior too use as recommended by Caron and Kramer (1989). The resulting theoretical concentrations for hydrogen sulphide and methyl mercaptan, 4.87 mg/l and 6.88 mg/l, respectively, were below their respective solubility limits in water (Windholz, 1983). The resulting theoretical concentrations for dimethyl sulphide and dimethyl disulphide, 3.28 mg/l and 4.06 mg/l, respectively, were also below their solubility limits (A solubility test, in which dimethyl sulphide and dimethyl disulphide were injected into water, indicated that dimethyl sulphide and dimethyl disulphide were indeed soluble in water to concentrations in excess of 20 mg/l). The pH of the standard mixture was adjusted to approximately 3.5 with hydrochloric acid

as required. The standard mixture was diluted 2, 5 and 10 times and analyzed to obtain data for the calibration curve. The resulting concentration of RSCs in the diluted samples corresponded to the range of interest for determining the removal rates for RSCs in an MBR.

To improve the accuracy and precision of the analytical method, thioanisole was added to each sample as previously described. The absolute peak areas for the RSCs were normalized against a common $\log_{10}$ peak area for thioanisole. The $\log_{10}$ peak area for thioanisole was calculated by averaging the $\log_{10}$ peak areas for thioanisole for all the samples analyzed in one series. The normalized peak area for each RSC was then calculated according to Equation A1-1. Normalizing the peak areas before developing the calibration curve increased the coefficient of determination (r^2) and reduced the standard error of the estimate associated with the calibration curve, thus increasing the accuracy of the analytical method and also reduced the standard error associated with the slope of the $\log_{10}$-$\log_{10}$ calibration curve increasing the precision of the analytical method.

$$\text{Normalized Peak Area for RSC} = 10^{\wedge}\left(\log_{10}\left(\text{Absolute Peak Area for RSC in Sample}\right) \times \left(\frac{\log_{10}\left(\text{Absolute Peak Area for Thioanisole in Sample}\right)}{\log_{10}\left(\text{Average Absolute Peak Area for Thioanisole in all Samples Analyzed}\right)}\right)\right) \quad \text{(A1-1)}$$

Results and Discussion

The chemiluminescence emitted in a flame photometric detector is theoretically proportional to the square of the amount of sulphur reaching the detector (i.e. linear relationship, with a slope of 2, between the $\log_{10}$ of the peak area obtained from the GC-

FPD and the $\log_{10}$ of the concentration of RSC injected) (Farwell and Barinaga, 1989). The calibration curves observed in the present study exhibited linear relationships between the $\log_{10}$ of the concentrations of each RSC injected and the $\log_{10}$ of their respective peak areas. However, the power law exponent (slope of $\log_{10}$-$\log_{10}$ calibration curve) for each RSC was less than 2. The deviation from the theoretical power law exponent of 2 is likely due to hydrocarbon quenching, which occurs when some of the light emitted by the sulphur species is adsorbed by the carbon dioxide present in the flame when organic sulphur compounds are injected into the GC-FPD (Patterson and Howe, 1978). Power law exponents have been reported to vary from one (directly proportional to the concentration of sulphur species), to the theoretical exponent of two (Peppard, 1988; Sola et al., 1997; Patterson et al., 1978). The power law exponent for the RSCs investigated in the present study appeared to decrease with an increase in the fraction of carbon associated with each RSC indicating that hydrocarbon quenching increased with the fraction of carbon associated with each RSC (Table A1-1). Self-quenching, which can occur when injecting high concentrations of sulphur compounds into a GC-FPD, was not a problem over the range of concentrations investigated. Self quenching results in a non linear slope for the $\log_{10}$-$\log_{10}$ calibration curve (Patterson et al., 1978).

The concentration of each RSC in a sample was calculated according to Equation A1-2. The exponent P corresponds to the power law exponent for the individual RSCs examined.

$$\text{Concentration (mg/l)} = \left(\left(\frac{\text{Normalized Peak Area for Sample}}{\text{Normalized Peak Area for Standard}} \right) \times \left(\text{Concentration of Standard (mg/l)} \right)^{P} \right)^{(1/P)} \qquad \text{(A1-2)}$$

Good and consistent recoveries were observed for all RSCs, in all aqueous matrices examined and over the range of concentrations examined. The average recoveries for hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide, for samples collected from all matrices examined, were 105 ± 15 %, 107 ± 17 %, 101 ± 12 % and 97 ± 9 %, respectively (n=16; 90 % confidence interval). The relationships between the concentration of RSCs and their respective normalized peak areas are not linear. Consequently, the 90 % confidence interval for the concentration measurements of each RSC varies with the concentration of the RSC measured. The range of the 90 % confidence interval for the concentration measurements of each RSC, over the range of concentrations investigated, is listed in Table A1-1. The precision of the concentration measurements for dimethyl sulphide and dimethyl disulphide is satisfactory. However, the precision of the concentration measurements for hydrogen sulphide and methyl mercaptan is significantly lower. The lower precision associated with the concentration measurements for these compounds is likely due to their highly volatile nature and the resulting effect on the sampling error. The precision can be improved by analyzing multiple samples.

Poor recoveries were initially observed for hydrogen sulphide, methyl mercaptan and dimethyl disulphide in tap water. The resulting recoveries for hydrogen sulphide and methyl mercaptan were less than 41 % and 88 % respectively, and these decreased with the amount of RSCs injected. The recovery for dimethyl disulphide was greater than 160 %. The low recovery for hydrogen sulphide was attributed to the reaction and precipitation of hydrogen sulphide with the copper contained in the tap water. The low recovery for methyl mercaptan and the high recovery for dimethyl disulphide was attributed to the oxidation of methyl mercaptan to dimethyl sulphide in tap water. Similar observations were reported by Saunders (1995). Good recoveries were observed when the tap water was purged with hydrogen sulphide and methyl mercaptan, to precipitate the copper and remove the oxidizing potential of the tap water, and then stripped of these gases prior to spiking with RSCs to determine the recoveries.

Table A1 – 1

Calibration Curve Results

RSC	Range	Power Law [1]Exponent	Confidence Interval for the Concentration Measurements	
	(mg/l)	(-)	(log_{10} signal) [1,2]	(mg/l) [1,3]
Hydrogen Sulphide	0.49 - 4.87	1.92 ± 0.17	± 0.26	± 0.15 - ± 1.52
Methyl Mercaptan	0.69 - 6.88	1.90 ± 0.16	± 0.14	± 0.12 - ± 1.18
Dimethyl Sulphide	0.33 - 3.28	1.66 ± 0.15	± 0.12	± 0.02 - ± 0.18
Dimethyl Disulphide	0.41 - 4.06	1.72 ± 0.20	± 0.11	± 0.06 - ± 0.59

Notes:

1 The "±" corresponds to the 90 % confidence interval from the 5 calibration curves using distilled water as solution matrix.

2 90 % confidence interval for the concentration measurements expressed as Log_{10} normalized peak area.

3 90 % confidence interval for the concentration measurements expressed as mg/l, at the lower and upper range of concentrations examined.

Conclusions

1. Direct injection of aqueous samples into a CG-FPD can be used to measure the concentration of RSCs in aqueous matrices. Consistent results and relatively good recoveries were observed for all aqueous matrices examined over the range of concentrations examined.
2. The analytical method requires only a small sample volume (2 ml), sample preparation and analysis can be completed within 20 minutes and no complex sampling apparatus is required.
3. Samples must be filtered with glass fiber filters to insure proper recoveries.
4. The exponent in the power law relationship between normalized peak area and concentration is different for each RSC. The power law exponent appears to decrease with the organic fraction associated with each RSC. The power law exponent for

hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide are 1.92, 1.90, 1.66 and 1.72, respectively.

5. The combination of periodic cleaning of the injection port, split injection and the use of a wide bore capillary chromatograph column prevented the detector flame from being extinguished and the occurrence of ghost peaks.

References listed along with those from the main body of text.

Appendix 2 – Characteristics of Evaporator Condensate

A2.1 Evaporator Condensate from the Western Pulp Limited Partnership Bleached Kraft Pulp Mill

The foul evaporator condensate from the Western Pulp Limited Partnership bleached kraft pulp mill in Squamish, Canada, were characterized over a two year period. The first monitoring period lasted four months from January 1997 to April, 1997. The second monitoring period lasted twelve months from March, 1998 to February, 1999.

Shipments of evaporator condensate were sent to the research laboratory where the bench scale MBR was located once per week during the monitoring periods. The evaporator condensate was collected from the "Contaminated Condensate Seal Tank" and consisted of condensate produced in the 6^{th} effect after heater and in the second stage of the surface condenser in the evaporation plant. At the Western Pulp Limited Partnership mill, the evaporator condensate flow to the Contaminated Seal Tank accounts for approximately 10 % of the total evaporator condensate flow. The total evaporator condensate flow is approximately 6.6 m^3/min (11.6 m^3/admt).

During the first monitoring period, the evaporator condensate shipments were sampled and analyzed for methanol, hydrogen sulphide, methyl mercaptan, dimethyl sulphide, dimethyl disulphide, pH and conductivity. During the second monitoring period, the evaporator condensate shipments were also characterized for TOC. Evaporator condensate shipments that had a conductivity greater than 300 μS were discarded. A high conductivity indicated the presence of a significant amount of black liquor entrainment into the evaporator condensate (personal communication, Taylor J., 1996, Western Pulp Limited Partnership, Squamish, Canada). Four of the shipments received during the two monitoring periods had a conductivity higher than 300 μS. In addition to having a higher conductivity, the color of the evaporator condensate in these shipments was also much darker (i.e. almost black as opposed to the usual light brown). No

significant process disruptions were recorded at the Western Pulp Limited Partnership mill on these occasions. The analytical methods used for the analysis of the evaporator condensate are presented in Appendix 1. The characteristics of the evaporator condensate are presented in Table A2-1.

Table A2-1 Characteristics of Evaporator Condensate from Western Pulp Limited Partnership Bleached Kraft Pulp Mill

	Methanol	TOC	TOC (filt)	TOC (solid)	MeOH as TOC	H2S	CH3SH	DMS	DMDS	RSC as TOC	RSC as TOC
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	%
21-Jan-97	519	-	-	-	-	-	-	-	-	-	-
5-Feb-97	600	-	-	-	-	-	-	-	-	-	-
29-Jan-97	583	-	-	-	-	-	-	-	-	-	-
13-Feb-97	552	-	-	-	-	-	-	-	-	-	-
19-Feb-97	580	-	-	-	-	67	56	45	30	39	-
26-Feb-97	616	-	-	-	-	75	84	49	24	46	-
8-Mar-97	634	-	-	-	-	51	28	31	22	25	-
12-Mar-97	680	-	-	-	-	75	89	54	32	51	-
10-Apr-97	610	-	-	-	-	53	51	18	7	22	-
16-Apr-97	560	-	-	-	-	81	54	38	18	33	-
Average	593	-	-	-	-	67	60	39	22	36	-
+/- (90%)	65	-	-	-	-	20	37	22	15	19	-
5-Mar-98	1031	-	-	-	-	71	80	28	8	33	-
15-Apr-98	776	-	-	-	-	71	90	39	14	41	-
22-Apr-98	1212	-	-	-	-	75	73	37	14	36	-
27-May-98	909	-	-	-	-	89	78	25	12	32	-
2-Jul-98	987	-	-	-	-	-	-	-	-	-	-
8-Jul-98	1258	580	-	-	81%	-	-	-	-	-	-
15-Jul-98	980	447	435	-	82%	73	67	30	8	30	7%
22-Jul-97	1206	588	541	8%	77%	90	82	38	11	38	6%
29-Jul-98	1193	634	576	9%	71%	78	53	34	7	28	4%
16-Sep-98	1068	621	523	16%	64%	-	-	-	-	-	-
23-Sep-98	858	462	427	8%	70%	-	-	-	-	-	-
30-Sep-98	1174	600	585	3%	73%	-	-	-	-	-	-
7-Oct-98	945	531	453	15%	67%	-	-	-	-	-	-
14-Oct-98	703	443	380	14%	60%	69	77	37	9	36	8%
4-Nov-98	1204	582	488	16%	78%	-	-	-	-	-	-
12-Nov-98	990	541	409	24%	69%	-	-	-	-	-	-
18-Nov-98	759	520	460	12%	55%	-	-	-	-	-	-
2-Dec-98	834	317	286	10%	99%	-	-	-	-	-	-
9-Dec-98	939	474	437	8%	74%	123	133	63	16	62	13%
16-Dec-98	617	406	360	11%	57%	59	40	36	30	32	8%
30-Dec-98	945	560	473	16%	63%	-	-	-	-	-	-
6-Jan-99	837	473	389	18%	66%	-	-	-	-	-	-
13-Jan-99	882	437	436	0%	76%	-	-	-	-	-	-
20-Jan-99	852	571	487	15%	56%	-	-	-	-	-	-
27-Jan-99	895	479	418	13%	70%	-	-	-	-	-	-
2-Feb-99	906	432	330	24%	79%	-	-	-	-	-	-
10-Feb-99	1112	-	-	-	-	-	-	-	-	-	-
24-Feb-99	920	397	-	-	87%	61	94	62	9.1	50	13%
Average	964	504	445	12%	71%	78	79	39	13	38	8%
+/- (90%)	272	137	126	10%	17%	29	39	20	11	16	5%

The evaporator condensate shipments were also periodically analyzed for volatile and total suspended solids. Samples of foul evaporator condensate were analyzed for volatile suspended solids and total suspended solids on December 16, 1998, January 27, 1999 and Feb 24, 1999. The volatile suspended solids concentrations were 444 mg/L, 432 mg/L and 432 mg/L and the total suspended solids concentrations were 656 mg/L, 650 mg/L and 644 mg/L, respectively, for the three sampling dates. The observed suspended solids concentrations are higher than typically reported in evaporator condenste. The suspended solids concentration in evaporator condensate typically ranges from 30 to 70 mg/L (Blackwell et al., 1979). The higher suspended solids observed during the present study is likely due to the physical entrainment of solids during evaporation.

A summary of the characteristics of the evaporator condensate is presented in Table A2-2. As presented in the summary table, the characteristics of the evaporator condensate from the Western Pulp Limited Partnership bleached kraft pulp mill can be considered as typical for the pulp and paper industry.

Table A2-2 Summary of Characteristics of Evaporator Condensate from Western Pulp Limited Partnership Bleached Kraft Pulp Mill

Parameter	Average Value	Typical Value
Methanol (mg/L)		180-1200
Monitoring period year 1	593 ± 65	
Monitoring period year 2	964 ± 272	
Hydrogen Sulphide (mg/L)	78 ± 29	1-240
Methyl Mercaptan (mg/L)	79 ± 39	1-410
Dimethyl Sulphide (mg/L)	39 ± 20	1-15
Dimethyl Disulphide (mg/L)	13 ± 11	1-50
TOC (mg/L)	504 ± 137	
PH (-)	7.5-8	6.7-8.2

(* shipments with a conductivity higher than 300 µS were discarded)

(typical values from Blackwell et al., 1979)

When the shipments (one or two 20 L pails were delivered every week) of evaporator condensate were received from the Western Pulp mill, they were immediately sampled and characterized. The shipments were then preserved by acidifying the evaporator condensate to a pH of approximately 4 using HCl. The RSC contained in the evaporator condensate tend to be more stable under acidic conditions (Chen and Morris, 1972). The acidified evaporator condensate pail was then sealed and stored at a temperature of 4 °C to minimize any potential stripping of the volatile contaminants contained in the evaporator condensate. The evaporator condensate was transferred to a smaller 2 L sealed container, which was also stored at 4 °C, when fed to the MBR. This minimized the stripping of the volatile contaminants contained in the evaporator condensate and also minimized the exposure of the evaporator condensate to air. RSC can be abiotically oxidize in the presence of oxygen (Chen and Morris, 1972). The evaporator condensate were typically used as feed to the MBR within one week. Degradation tests indicated that the characteristics of the evaporator condensate did not change significantly during storage, except for hydrogen sulphide and methyl mercaptan. The concentrations of hydrogen sulphide and methyl mercaptan in the evaporator condensate decreased by approximately 50 % and 30 %, respectively, during storage. The decrease in the concentration of these RSC occurred within 2 days. The concentrations of hydrogen sulphide and methyl mercaptan did not further decrease after the first 2 days of storage.

The cleaner fraction of the evaporator condensate from the Western Pulp Limited Partnership bleached kraft pulp mill was also sampled and analyzed for the contaminants of concern. The cleaner fraction of the evaporator condensate flow accounts for the remaining 90 % of the total evaporator condensate flow. Samples of the cleaner evaporator condensate were collected from the "Combined Condensate Seal Tank" and consisted of condensate from the 6^{th} effect and from the surface condenser in the evaporation plant. Under current operating conditions, approximately 30 % to 50 % of the cleaner fraction of the condensate is reused as process feedwater at the Western Pulp Limited Partnership mill (personal communication, Taylor J., 1996, Western Pulp Limited Partnership, Squamish, Canada). The characteristics of the cleaner fraction of the evaporator condensate are presented in Table A2-3.

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Table A2-3

Characteristics of Cleaner Fraction of the Evaporator Condensate from Western Pulp Limited Partnership Bleached Kraft Pulp Mill

	Methanol	TOC	TOC (filt)	TOC (solid)	MeOH as TOC	H2S	CH3SH	DMS	DMDS	RSC as TOC	RSC as TOC
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	%
14-Oct-98	425	347	299	14%	46%	10	0.26	0.8	0.24	0.44	0.13%
16-Dec-98	375	305	282	8%	46%	10	0.2	1.1	0.25	0.54	0.18%
6-Jan-98	388	310	285	8%	47%	6	0.4	0.6	0.25	0.4	0.13%
Average	396	321	289	10%	46%	9	0.29	0.83	0.25	0.46	0.14%
+/- (90%)	15	6	3	1%	1%	5	0.23	0.58	0	0.17	0.06%

As presented in Table A2-3, the concentration of methanol in the cleaner fraction of the evaporator condensate is approximately 70 % less than that observed in the evaporator condensate from the Contaminated Seal Tank. In addition, methanol accounts for less of the TOC content in the cleaner fraction of the evaporator condensate compared to the evaporator condensate from the Contaminated Seal Tank. The concentration of hydrogen sulphide in the clean fraction of the evaporator condensate is approximately 90 % less than that observed in the evaporator condensate from the Contaminated Seal Tank and the concentration of methyl mercaptan, dimethyl sulphide and dimethyl disulphide in the cleaner fraction of the evaporator condensate is approximately 99 % less than that observed in the evaporator condensate from the Contaminated Seal Tank.

A2.2 Synthetic Evaporator Condensate

As discussed in Chapters 4, 5 and 6, synthetic evaporator condensate was used during the first three experiments. Synthetic evaporator condensate was used mainly because the very foul nature of real evaporator condensate made it difficult to work with them. As discussed in Section 2.2.1, real evaporator condensate contains a number of foul odorous compounds and HAP that can produce unpleasant or even hazardous working conditions in the area where this material is handled. Synthetic evaporator condensate was also used

to investigate the effect of the contaminant matrix present in real evaporator condensate, on the biological treatment of evaporator condensate for reuse as presented in Chapter 6.

The synthetic evaporator condensate contained methanol and RSC, in tap water, at concentrations similar to those observed in the evaporator condensate from the Contaminated Condensate Seal Tank at the Western Pulp Limited Partnership bleached kraft pulp mill. As presented in Section 2.1, methanol and RSC are the most abundant contaminants present in evaporator condensate. The synthetic evaporator condensate contained methanol, dimethyl sulphide and dimethyl disulphide at concentrations of 500 mg/L, 37 mg/L and 25 mg/L, respectively. The synthetic condensate did not contain hydrogen sulphide and methyl mercaptan because of the difficulty of solubilizing these gaseous RSC to specific concentrations in liquid. The concentration of methanol in the synthetic evaporator condensate corresponds to the concentration observed during the first part of the monitoring period. The synthetic condensate was stored at a temperature of 4 °C. A new batch of synthetic evaporator condensate was made every 2 to 3 days. There was no significant change in the concentration of methanol, dimethyl sulphide or dimethyl disulphide during storage.

Appendix 3 – Nutrient Solution

Nitrogen, phosphorus and a number of other trace nutrients (iron, calcium, potassium, magnesium, molybdenum, zinc, copper, cobalt, sodium) are required for the optimal growth of microorganisms in a biological treatment system. Grau (1991) reported that for each gram of BOD that is biologically consumed by a mixed culture of microorganisms, approximately 50, 10, 12, 6.2, 4.5, 3, 0.43, 1.16, 0.15, 0.13 and 0.05 mg of nitrogen, phosphorus, iron, calcium, potassium, magnesium, molybdenum, zinc, copper, cobalt and sulphate, respectively, are required to ensure non-nutrient limiting conditions. For sulphur-oxidizing microorganisms, the type and concentration of nutrients reported to be required for optimal growth is not consistent (Kargi and Robinson, 1982, 1984; Kargi, 1987, Shrives and Brock, 1973). The American Type Culture Collection (ATCC) recommends the use of a nutrient solution containing $MgSO_4.7H_2O$, $MgCl.6H_2O$, $CaCl_2.7H_2O$, $FeCl_3.6H_2O$, $MnCl_2.4H_2O$, $Na_2B_4O_7.10H_2O$, $ZnSO_4.7H_2O$, $CoCl_2.6H_2O$ and $Na_2MoO_4.2H_2O$ at concentrations of 25, 270, 70, 20, 1.8, 4.5, 0.2, 0.05 and 0.03 mg/L, respectively, to provide non-nutrient limiting conditions for the growth of sulphur-oxidizing microorganisms. To provide optimal conditions for the growth of both organic and sulphur-oxidizing microorganisms, the more stringent of the nutrient requirements proposed by Grau (1991) and the ATCC were used.

The synthetic evaporator condensate used in experiments 1 to 3, presented in Chapters 4 to 6, did not contain any of the nutrients required for growth. For nitrogen and phosphorus the requirements reported by Grau (1991) were used. The nitrogen and phosphorus requirements were based on an influent methanol concentration of 1200 mg/L. This corresponded to the maximum expected concentration for methanol in the evaporator condensate (Blackwell et al., 1979). It was assumed that 1.5 mg of BOD was equivalent to 1 mg of methanol (i.e. complete oxidation of methanol to CO_2 and H_2O). Nitrogen was added as ammonia nitrogen. Ammonium nitrate was used as the source of ammonia nitrogen. The nitrate component of the ammonium nitrate was assumed not to contribute a significant amount of nitrogen as nutrient since nitrate nitrogen is

significantly less readily available than ammonia nitrogen (Pitter and Chudoba, 1990). To determine if ammonia nitrogen was being removed from the system by nitrification, the concentration of NO_x in the MBR was monitored. The results indicated that nitrification was not occurring. Phosphorus was added as orthophosphate. Orthophosphate is an easily available form of phosphorus for microorganisms (Metcalf and Eddy, 1991). Potassium orthophosphate was used as the source of orthophosphate. The requirements for nitrogen and phosphorous were increased by approximately 50 % to ensure non-limiting conditions.

For the trace nutrients, the more stringent ATCC requirements were used.

During the preparation of the nutrient solution, phosphate solids were formed. These solids were removed from the nutrient solution by allowing the solids to settle overnight and then decanting the supernatant. To account for the amount of phosphorus removed with the precipitate, the amount of KH_2PO_4 added to the nutrient solution was doubled. This produced a solution with the required amount of orthophosphate. The formation of solids and their subsequent removal did not significantly affect the concentration of the other compounds in the nutrient solution.

Real evaporator condensate contains some of the nitrogen required for the growth of microorganisms (Welander et al., 1999). However, the type of the nitrogen compounds present in evaporator condensate are not in a form that is readily available to microorganisms. To ensure comparable results for the experiments using synthetic and real evaporator condensate, the same nutrient solution was added to the MBR when both synthetic and real evaporator condensate were used as feed.

The concentration of the different nutrients, per litre of evaporator condensate, is listed in Table A3-1.

Table A3-1

Characteristics of Nutrient Solution

Nutrients	Approximate Nutrient Concentration per Litre of Evaporator Condensate (mg/L)
NH_4NO_3	850
KH_2PO_4	130 (*300)
$MgSO_4.7H_2O$	25
$MgCl.6H_2O$	270
$CaCl_2.7H_2O$	70
$FeCl_3.6H_2O$	20
$MnCl_2.4H_2O$	1.8
$Na_2B_4O_7.10H_2O$	4.5
$ZnSO_4.7H_2O$	0.2
$CoCl_2.6H_2O$	0.05
$Na_2MoO_4.2H_2O$	0.03

(* adding KH_2PO_4 to a concentration of 300 mg/L in the nutrient mixture resulted in a KH_2PO_4 of approximately 130 mg/L in the nutrient solution supernatant)

Nutrients were added in excess during the present study. Further research is required to determine the nutrient requirements for treating evaporator condensate using a high temperature MBR. Optimizing the nutrient requirements is necessary to determine the exact chemical costs to treat evaporator condensate for reuse.

Appendix 4 – Data Collected During Feasibility Experiment

Appendix 4 contains the data collected during Parts I and II of the feasibility experiment presented in Chapter 4.

A4.1 Part I - Feasibility of Biologically Removing Methanol and RSC Using a High Temperature MBR

The concentrations of MLVSS measured during Part I of the feasibility experiment are presented in Table A4.1.

The results from the investigation of the removal of methanol, monitored during Part I for selected batch feed cycles, are presented in Tables A4.2 to A4.17. For these tables, the parameter K corresponds to the zero order coefficient for the biological removal of methanol (mg/L•minute), as presented in Equation 4.4, and the parameter Co corresponds to the methanol concentration in the MBR at the start of the selected batch feed cycle (mg/L). The results presented in Tables A4.15 to A4.17 are for methanol removal at different RSC concentrations.

The results from the investigation of the removal of RSC, monitored during Part I for selected batch feed cycles, are presented in Tables A4.18 to A4.21. For these tables, the parameter K corresponds to the first order coefficient for the removal of RSC (/minute), as presented in Equation 4.5, and the parameter Co corresponds to the RSC concentration in the MBR at the start of the selected batch feed cycle (mg/L).

The results from the investigation of the abiotic removal of methanol and RSC, monitored during Part I using clean water, are presented in Tables A4.22 to A4.26. For these tables, the parameter K corresponds to the first order coefficient for the stripping of methanol and RSC (/minute), as presented in Equations 4.2 and 4.6, respectively.

The R^2 value, presented in the following tables, is the coefficient of determination for linear regression. Similarly, the I^2 value is the correlation index square for non-linear regression.

Table A4.1
MLVSS Concentration in MBR during Part I of Feasibility Experiment

Date	MLVSS (mg/L)
2-Sep-97	7272
3-Sep-97	6944
5-Sep-97	6364
6-Sep-97	7236
7-Sep-97	6764
11-Sep-97	6424
12-Sep-97	6838
16-Sep-97	7040
23-Sep-97	6888
24-Sep-97	6860
26-Sep-97	6692
27-Sep-97	6788
29-Sep-97	6900
6-Oct-97	3480
7-Oct-97	4348
12-Oct-97	3036
14-Oct-97	2928
16-Oct-97	3100
17-Oct-97	3108
23-Oct-97	3092
27-Oct-97	2960
30-Oct-97	2768
1-Nov-97	2700
6-Nov-97	2880
12-Nov-97	2716
17-Nov-97	2900
27-Nov-97	2868
4-Dec-97	3072

Table A4.2 - Methanol Removal in MBR September 6, 1997

Time (min)	Methanol (mg/L)	Co	72.9
		K	1.4
5	65.0	R^2	0.991
20	46.7		
35	19.1		
50	2.0		
65	n.d.		

Table A4.3 - Methanol Removal in MBR September 23, 1997

Time (min)	Methanol (mg/L)	Co	85.5
		K	1.4
5	80.9	R^2	0.968
20	56.3		
35	39.0		
50	6.4		
65	1.5		

Table A4.4 - Methanol Removal in MBR September 30, 1997

Time (min)	Methanol (mg/L)	Co	73.6
		K	1.5
5	67.1	R^2	0.997
20	44.4		
35	20.5		
50	2.2		
65	n.d.		

Table A4.5 - Methanol Removal in MBR October 12, 1997

Time (min)	Methanol (mg/L)	Co	76.3
		K	1.4
5	68.2	R^2	0.997
20	50.0		
35	25.1		
50	5.3		
65	n.d.		

Table A4.6 - Methanol Removal in MBR October 16, 1997

Time (min)	Methanol (mg/L)	Co	72.6
		K	1.4
5	64.1	R^2	0.982
20	48.3		
35	18.1		
50	2.6		
65	n.d.		

Table A4.7 - Methanol Removal in MBR October 20, 1997

Time (min)	Methanol (mg/L)	Co	99.3
		K	1.6
5	89.1	R^2	0.987
20	72.1		
35	40.2		
50	19.6		
65			

Table A4.8 - Methanol Removal in MBR October 24, 1997

Time (min)	Methanol (mg/L)	Co	99.4
		K	1.6
5	89.0	R^2	0.988
20	71.6		
35	39.3		
50	18.2		

Table A4.9 - Methanol Removal in MBR November 1, 1997

Time (min)	Methanol (mg/L)	Co	74.9
		K	1.4
5	65.7	R^2	0.992
20	49.0		
35	27.1		
50	2.2		
60	n.d.		

Table A4.10 - Methanol Removal in MBR November 14, 1997

Time (min)	Methanol (mg/L)	Co	80.9
		K	1.6
5	71.1	R^2	0.995
20	52.6		
35	25.6		
50	1.7		

Table A4.11 - Methanol Removal in MBR December 4, 1997

Time (min)	Methanol (mg/L)	Co	80.1
		K	1.5
5	71.3	R^2	0.995
20	53.3		
35	26.8		
50	3.5		
60	0.0		

Table A4.12 - Methanol Removal in MBR November 11, 1997 (RSC Concentration in Feed Increased Two Times)

Time (min)	Methanol (mg/L)	Co	101.5
		K	1.4
5	91.8	R^2	0.984
20	75.0		
35	60.2		
50	30.6		
60	18.5		

Table A4.13 - Methanol Removal in MBR November 11, 1997 (RSC Concentration in Feed Increased Four Times)

Time (min)	Methanol (mg/L)	Co	117.0
		K	1.4
5	108.8	R^2	0.982
20			
35	74.3		
50	42.9		
65	28.5		

Table A4.14 - Methanol Removal in MBR November 11, 1997 (RSC Concentration in Feed Increased Eight Times)

Time (min)	Methanol (mg/L)	Co	138.0
		K	1.6
5	128.2	R^2	0.970
20	112.3		
35	84.4		
50	49.5		
65	41.1		

Table A4.15 - RSC Removal in MBR
November 1, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	7.0	2.6
25	4.7	2.0
40	2.6	1.1
55	2.9	1.5
Co	8.1	2.9
K	0.019	0.012
I^2	0.976	0.972

Table A4.16 - RSC Removal in MBR
November 10, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	4.5	2.3
25	3.0	1.6
40	2.8	1.5
55	1.6	0.9
Co	5.5	2.7
K	0.021	0.019
I^2	0.933	0.955

Table A4.17 - RSC Removal in MBR
November 14, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	4.6	2.2
25	3.2	1.6
40	2.3	1.3
55	1.7	0.6
Co	5.5	3.2
K	0.021	0.020
I^2	0.997	0.897

Table A4.18 - RSC Removal in MBR
November 27, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	4.7	2.4
25	3.4	1.9
40	2.4	1.1
55	2.1	1.2
Co	5.6	2.7
K	0.019	0.017
I^2	0.977	0.8285

Table A4.19 - RSC Removal in MBR
December 1, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	6.2	2.1
25	3.8	1.3
40	3.4	1.4
55	2.2	1.0
Co	7.3	2.3
K	0.021	0.015
I^2	0.951	0.859

Table A4.20 - RSC Removal in MBR
December 2, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	5.8	2.4
25	4.4	2.0
40	2.9	1.4
55	2.1	1.1
Co	7.4	2.9
K	0.023	0.018
I^2	0.993	0.990

Table A4.21 - RSC Removal in MBR December 4, 97

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	4.8	1.8
25	3.8	1.3
40	2.9	1.0
55	2.2	0.8
Co	5.8	2.1
K	0.018	0.018
I^2	0.998	0.994

Table A4.22 - Methanol Removal in MBR April 4, 98(Clean Water Stripping Test I)

Time (min)	Methanol (mg/L)	Co	88.9
5	89.1	K	0.00024
20	89.2	I^2	0.359
35	88.5		
50	85.6		
65	86.4		
80	88.4		
95	86.8		
110	86.8		

Table A4.23 - Methanol Removal in MBR April 4, 98(Clean Water Stripping Test II)

Time (min)	Methanol (mg/L)	Co	184.6
5	184.2	K	0.00021
71	181.4	I^2	0.792
80	182.6		
95	181.4		
110	179.4		

Table A4.24 - Methanol Removal in MBR April 4, 98(Clean Water Stripping Test III)

Time (min)	Methanol (mg/L)	Co	244.0
5	244.7	K	0.00006
70	207.0	I^2	0.047
80	242.6		
95	245.1		

Table A4.25 - RSC Removal in MBR April 4, 98(Clean Water Stripping Test I)

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	6.8	3.3
25	4.1	2.1
40	2.9	1.6
55	2.3	1.3
Co	8.0	3.7
K	0.023	0.019
I^2	0.976	0.953

Table A4.26 - RSC Removal in MBR April 4, 98(Clean Water Stripping Test II)

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	6.0	2.9
25	5.5	2.4
40	3.2	1.6
55	2.5	1.4
Co	8.0	3.5
K	0.021	0.017
I^2	0.937	0.970

Table A4.27 - RSC Removal in MBR April 4, 98(Clean Water Stripping Test III)

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	6.1	3.0
25	4.4	2.2
40	3.8	1.9
55	2.4	1.3
Co	7.5	3.6
K	0.02	0.018
I^2	0.963	0.975

A4.2 Part II - Enhanced Biological Oxidation of Reduced Sulphur Compounds

The concentrations of mixed liquor volatile suspended solids measured during Part II of the feasibility experiment are presented in Table A4.28.

The results from the investigation of the removal of methanol, monitored during Part II for selected batch feed cycles, are presented in Table sA4.31 to A4.39. For these tables, the parameter K corresponds to the zero order coefficient for the biological removal of methanol (mg/L•minute), as presented in Equation 4.4, and the parameter Co corresponds to the methanol concentration in the MBR at the start of the selected batch feed cycle (mg/L).

The results from the investigation of the removal of RSC, monitored during Part II for selected batch feed cycles, are presented in Tables A4.40 to A4.53. For these tables, the parameter K corresponds to the sum of the first order coefficient for the biological removal and the stripping of RSC (/minute), as presented in Equation 4.7, and the parameter Co corresponds to the RSC concentration in the MBR at the start of the selected batch feed cycle.

The results from the investigation of the abiotic removal of RSC, monitored during Part II using clean water at different operating pH, are presented in Tables A4.54 to A4.61. For these tables, the parameter K corresponds to the first order coefficient for the stripping of methanol and RSC (/minute), as presented in Equations 4.2 and 4.6, respectively.

The R^2 value, presented in the following tables, is the coefficient of determination for linear regression. Similarly, the I^2 value is the correlation index square for non-linear regression.

Table A4.28
MLVSS Concentration in MBR during Part II of Feasibility Study

Date	MLVSS (mg/L)
1-Dec-97	2200
12-Dec-97	2216
2-Jan-98	1380
10-Jan-98	1244
17-Jan-98	1122
30-Jan-98	1156
10-Feb-98	708
22-Feb-98	648
1-Mar-98	500
10-Mar-98	392
20-Mar-98	357

Table A4.29 - Methanol Removal in MBR pH 6, December 10, 1997

Time (min)	Methanol (mg/L)	Co	117.37
5	107.64	K	1.37
20	91.56	R^2	0.9837
35	75.23		
50	43.82		
65	28.69		

Table A4.30 - Methanol Removal in MBR pH 6, December 12, 1997

Time (min)	Methanol (mg/L)	Co	110.85
5	100.64	K	1.43
20	84.56	R^2	0.9879
35	65.19		
50	34.51		
65	17.89		

Table A4.31 - Methanol Removal in MBR pH 6, December 20, 1997

Time (min)	Methanol (mg/L)	Co	112.95
5	104.59	K	1.479
20	84.6	R^2	0.9869
35	64.56		
50	32.46		
65	19.74		

Table A4.32 - Methanol Removal in MBR pH 4, January 16, 1998

Time (min)	Methanol (mg/L)	Co	111.21
5	109.67	K	0.4282
20	102.48	R^2	0.9798
35	96.46		
50	87.50		
65	85.04		

Table A4.33 - Methanol Removal in MBR pH 4, January 17, 1998

Time (min)	Methanol (mg/L)	Co	140.51
5	134.75	K	0.4329
20	134.75	R^2	0.9257
35	128.31		
50	118.67		
65	110.32		

Table A4.34 - Methanol in MBR pH 4, February 1, 1998

Time (min)	Methanol (mg/L)	Co	108.98
10	104.12	K	0.4712
55	83.54	R^2	0.9993
75	73.31		

Table A4.35 - Methanol in MBR pH 3, February 24, 1998

Time (min)	Methanol (mg/L)	Co	587.19
5	595	K	0.0476
20	577	R^2	0.0239
35	592		
50	573		
65	585		
80	589		

Table A4.36 - Methanol in MBR pH 3, February 26 , 1998

Time (min)	Methanol (mg/L)	Co	575.19
5	578	K	0.0437
20	573	R^2	0.0043
35	567		
50	584		
65	572		
80	574		

Table A4.37 - Methanol in MBR pH 3, March 4, 1998

Time (min)	Methanol (mg/L)	Co	557.01
5	554	K	0.059
20	562	R^2	0.1534
35	550		
50	555		
65	555		
80	551		

Table A4.38 - RSC Removal in MBR pH 6, December 3, 1997

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	4.4	1.8
25	3.3	1.3
40	2.7	1.2
55	1.9	0.7
Co	5.3	2.1
K	0.018	0.019
I^2	0.986	0.924

Table A4.39 - RSC Removal in MBR pH 6, December 5, 1997

Time (min)	DMS (mg/L)	DMDS (mg/L)
10	4.7	1.8
25	3.3	1.3
40	2.2	0.9
55	2.0	0.8
Co	5.6	2.1
K	0.021	0.019
I^2	0.968	0.982

Table A4.40 - RSC Removal in MBR pH 4,January 5, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	7.9	1.8
20	6.3	1.3
35	3.9	0.8
50	2.2	0.5
65	1.4	n.d.
80	0.9	n.d.
95	0.6	n.d.
110	0.4	n.d.
Co	10.3	2.2
K	0.030	0.029
I^2	0.996	0.999

Table A4.41 - RSC Removal in MBR pH 4,January 9, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	4.5	1.9
20		
35	1.7	0.7
50	1.1	0.4
65	0.9	0.4
Co	4.9	2.0
K	0.028	0.029
I^2	0.980	0.960

Table A4.42 - RSC Removal in MBR pH 4,January 11, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	4.4	1.8
20	2.9	0.9
35	1.7	0.7
50	1.0	0.4
65	0.7	n.d.
80	0.4	n.d.
Co	4.7	2.0
K	0.028	0.032
I^2	0.989	0.995

Table A4.43 - RSC Removal in MBR pH 4, January 11, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	8.1	2.7
20	6.7	2.5
35	3.7	1.1
50	2.6	0.9
65	1.6	0.4
80	1.2	n.d.
95	0.8	n.d.
Co	9.9	3.4
K	0.027	0.029
I^2	0.992	0.970

Table A4.44 - RSC Removal in MBR pH 4,January 16, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	7.7	2.5
20	4.3	1.7
35	2.5	1.0
50	1.7	0.6
65	1.1	
Co	8.5	3.0
K	0.032	0.032
I^2	0.993	0.998

Table A4.45 - RSC Removal in MBR pH 4,January 16, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	6.0	2.3
20	3.9	1.6
35	2.3	0.4
50	1.5	0.5
65	0.9	0.3
80	0.6	n.d.
Co	7.0	2.4
K	0.031	0.031
I^2	0.999	0.901

Table A4.46 - RSC Removal in MBR pH 4, January 24, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	6.9	3.2
20		2.3
35	2.2	1.4
50	1.3	0.5
65	1.0	0.5
Co	7.6	4.1
K	0.033	0.034
I^2	0.983	0.951

Table A4.47 - RSC Removal in MBR pH 3, February 24, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	7.5	2.9
20	3.7	1.4
35	2.2	0.8
50	1.0	0.4
65	0.6	0.2
Co	8.9	3.5
K	0.041	0.042
I^2	0.996	0.998

Table A4.48 - RSC Removal in MBR pH 3, March 2, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	7.3	3.2
20	4.0	1.5
35	2.2	0.8
50	1.1	0.2
65	0.6	
Co	9.2	3.7
K	0.042	0.044
I^2	0.999	0.997

Table A4.49 - RSC Removal in MBR pH 3, March 5, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	11.0	4.8
20	8.4	3.2
35	6.7	2.3
50	4.9	1.3
65	3.8	1.1
Co	12.0	5.4
K	0.018	0.026
I^2	0.998	0.999

Table A4.50 - RSC Removal in MBR pH 3, March 10, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	8.4	3.2
20	6.3	1.9
35	4.7	1.4
50	3.5	0.7
65	2.5	0.6
Co	9.4	3.6
K	0.020	0.029
I^2	0.999	0.971

Table A4.51 - RSC Removal in MBR pH 3,March 15, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
9	8.0	3.1
20	6.7	1.9
35	4.3	1.1
50	3.8	1.0
65	3.1	0.6
Co	9.0	3.5
K	0.017	0.027
I^2	0.960	0.959

Table A4.52 - RSC Removal in MBR pH 3,March 19, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	8.5	3.4
20	7.1	2.6
35	5.1	1.8
50	4.3	1.5
65	3.2	0.9
Co	9.4	4.0
K	0.016	0.022
I^2	0.990	0.980

Table A4.53 - Clean Water Stripping pH 6, March 20, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	5.1	2.8
20	4.4	2.2
35	3.1	2.0
50	2.0	1.3
65	1.5	1.1
Co	6.2	3.2
K	0.021	0.017
I^2	0.983	0.967

Table A4.54 - Clean Water Stripping pH 6, March 21-a, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	4.5	2.3
20	3.5	1.2
35	2.8	1.1
50	2.0	0.9
65	1.4	0.6
Co	5.21	2.2
K	0.02	0.019
I^2	0.985	0.939

Table A4.55 - Clean Water Stripping pH 6, March 21-b, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	4.5	2.7
20	3.5	1.6
35	2.2	1.1
50	1.7	1.0
65	1.1	1.0
Co	5.2	2.5
K	0.023	0.017
I^2	0.988	0.8691

Table A4.56 - Clean Water Stripping pH 4, March 21, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	5.0	3.1
20	4.2	1.8
35	3.2	1.5
50	1.8	1.2
65	1.4	1.1
Co	6.12	2.9
K	0.022	0.017
I^2	0.967	0.931

Table A4.57 - Clean Water Stripping pH 4, March 22, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	4.7	1.8
20	3.2	1.0
35	2.8	0.8
50	1.6	0.5
65	1.1	0.5
Co	5.5	1.8
K	0.025	0.021
I^2	0.971	0.93

Table A4.58 - Clean Water Stripping pH 3, March 22-a, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	5.9	2.3
20	3.9	1.7
35	3.4	1.3
50	2.2	1.2
65	1.7	0.72
Co	6.4	2.5
K	0.021	0.018
I^2	0.098	0.968

Table A4.59 - Clean Water Stripping pH 3, March 22-b, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	5.4	3.0
20	3.6	2.1
35	2.6	1.4
50	2.0	1.2
65		
Co	5.8	3.3
K	0.022	0.027
I^2	0.991	0.985

Table A4.60 - Clean Water Stripping pH 3, March 23, 1998

Time (min)	DMS (mg/L)	DMDS (mg/L)
5	6.6	3.4
20	4.4	2.1
35	3.3	1.7
50	2.6	1.3
65	1.7	1.0
Co	7.1	3.4
K	0.021	0.019
I^2	0.992	0.978

Appendix 5 – Data Collected During Experiment Investigating the Effect of Operating Temperature on the Biological Removal of Methanol

Appendix 5 contains the data collected during Parts I and II, of the experiment investigating the effects of the operating temperature on the biological removal of methanol, presented in Chapter 5.

A5.1 Part I: Effect of Elevated Operating Temperatures on Methanol Removal Kinetics.

The daily volume of evaporator condensate treated, the ultrafiltration membrane flux, the concentration of MLVSS and the daily volume of sludge wasted, measured during Part I are presented in Tables A5.41 to A5.44.

The results from the investigation of the removal of methanol, monitored during Part I for selected batch feed cycles, are presented in Tables A5.1 to A5.32. For these tables, the parameter K corresponds to the zero order coefficient for the biological removal of methanol (mg/L•minute), as presented in Equation 4.4, and the parameter Co corresponds to the methanol concentration in the MBR at the start of the selected batch feed cycle (mg/L).

The results from the investigation of the abiotic removal of methanol, monitored during Part I using inactivated biomass, are presented in Tables A5.33 to A5.40. For these tables, the parameter K corresponds to the first order coefficient for the stripping of methanol (/minute) as presented in Equations 4.2.

The R^2 value, presented in the following tables, is the coefficient of determination for linear regression. Similarly, the I^2 value is the correlation index square for non-linear regression.

The observed growth yields, for the operating temperatures investigated, are presented in Tables A5.41 to A-44.

Table A5.1 – Methanol Removal in MBR, Temperature 55 °C, January 10, 1998

Time (min)	Methanol (mg/L)	Co	82.3
		K	1.14
5	77.9	R^2	0.995
15	65.2		
35	41.2		
50	22.6		
65	10.6		

Table A5.2 – Methanol Removal in MBR, Temperature 55 °C, January 13, 1998

Time (min)	Methanol (mg/L)	Co	85.45
		K	1.14
5	81.4	R^2	0.996
20	60.8		
35	44.5		
55	23.6		

Table A5.3 – Methanol Removal in MBR, Temperature 55 °C, January 15, 1998

Time (min)	Methanol (mg/L)	Co	84.2
		K	1.12
5	78.5	R^2	0.997
20	62.3		
35	43.5		
50	30.4		
65	10.4		

Table A5.4 – Methanol Removal in MBR, Temperature 55 °C, January 20, 1998

Time (min)	Methanol (mg/L)	Co	96.4
		K	1.28
5	90.9	R^2	0.999
20	69.9		
35	50.9		
55	26.6		

Table A5.5 – Methanol Removal in MBR, Temperature 55 °C, January 28, 1998

Time (min)	Methanol (mg/L)	Co	97.8
		K	1.19
5	95.8	R^2	0.973
20	72.1		
35	50.5		
60	30.1		

Table A5.6 – Methanol Removal in MBR, Temperature 60 °C, January 28, 1998

Time (min)	Methanol (mg/L)	Co	116.64
		K	0.78
5	113.0	R^2	0.993
20	102.0		
35	87.4		
55	75.0		

Table A5.7 – Methanol Removal in MBR, Temperature 60 °C, January 30, 1998

Time (min)	Methanol (mg/L)	Co	107
		K	0.80
5	103.8	R^2	0.999
20	90.2		
35	78.9		
60	59.3		

Table A5.8 – Methanol Removal in MBR, Temperature 60 °C, February 1, 1998

Time (min)	Methanol (mg/L)	Co	114.51
		K	0.97
5	109.6	R^2	1.000
20	94.8		
35	81.2		
60	56.2		

Table A5.9 – Methanol Removal in MBR, Temperature 60 °C, February 4, 1998

Time (min)	Methanol (mg/L)	Co	106
		K	1.06
5	98.5	R^2	0.993
20	87.9		
35	69.7		
50	51.4		
65	37.2		

Table A5.10 – Methanol Removal in MBR, Temperature 60 °C, February 10, 1998

Time (min)	Methanol (mg/L)	Co	109.5
		K	1.44
5	100.3	R^2	0.967
20	81.7		
35	66.7		
50	33.1		

Table A5.11 – Methanol Removal in MBR, Temperature 60 °C, February 17, 1998

Time (min)	Methanol (mg/L)	Co	108.34
		K	1.44
5	100.8	R^2	1.000
20	79.9		
35	58.2		
50	36.1		

Table A5.12 – Methanol Removal in MBR, Temperature 60 °C, February 22, 1998

Time (min)	Methanol (mg/L)	Co	94
		K	1.26
5	89.7	R^2	0.993
20	66.3		
35	48.9		
50	32.4		

Table A5.13 – Methanol Removal in MBR, Temperature 60 °C, February 25, 1998

Time (min)	Methanol (mg/L)	Co	109.83
		K	1.45
5	102.6	R^2	0.999
20	79.0		
35	57.9		
50	37.0		

Table A5.14 – Methanol Removal in MBR, Temperature 60 °C, February 28, 1998

Time (min)	Methanol (mg/L)	Co	103.8
		K	1.39
5	97.9	R^2	0.998
20	74.5		
35	54.9		
50	34.8		

Table A5.15 – Methanol Removal in MBR, Temperature 65 °C, March 4, 1998

Time (min)	Methanol (mg/L)	Co	100
		K	0.60
5	98.0	R^2	0.993
20	87.0		
35	78.1		
50	71.0		

Table A5.16 – Methanol Removal in MBR, Temperature 65 °C, March 4, 1998

Time (min)	Methanol (mg/L)	Co	121.5
		K	0.39
5	119.5	R^2	0.889
20	111.4		
35	110.1		
50	105.7		
60	94.3		

Table A5.17 – Methanol Removal in MBR, Temperature 65 °C, March 5, 1998

Time (min)	Methanol (mg/L)	Co	136.7
		K	0.56
5	133.1	R^2	0.952
20	128.1		
35	114.0		
50	109.7		

Table A5.18 – Methanol Removal in MBR, Temperature 65 °C, March 6, 1998

Time (min)	Methanol (mg/L)	Co	211.14
		K	0.62
5	209.0	R^2	0.971
20	195.9		
36	189.1		
50	183.6		
65	168.4		

Table A5.19 – Methanol Removal in MBR, Temperature 65 °C, March 12, 1998

Time (min)	Methanol (mg/L)	Co	157.02
		K	0.64
5	153.2	R^2	0.994
20	145.4		
36	134.2		
50	123.0		
65	116.1		

Table A5.20 – Methanol Removal in MBR, Temperature 65 °C, March 17, 1998

Time (min)	Methanol (mg/L)	Co	160.98
		K	0.68
5	159.6	R^2	0.953
20	148.7		
36	131.9		
50	124.7		
65	121.1		

Table A5.21 – Methanol Removal in MBR, Temperature 65 °C, March 24, 1998

Time (min)	Methanol (mg/L)	Co	156.6
		K	0.58
5	154.9	R^2	0.993
20	144.8		
35	134.8		
50	127.6		
65	120.3		

Table A5.22 – Methanol Removal in MBR, Temperature 65 °C, March 30, 1998

Time (min)	Methanol (mg/L)	Co	138.95
		K	0.63
5	134.8	R^2	0.996
20	127.7		
35	117.1		
50	107.8		
65	97.8		

Table A5.23 – Methanol Removal in MBR, Temperature 70 °C, April 1, 1998

Time (min)	Methanol (mg/L)	Co	104.5
		K	0.44
5	103.0	I^2	0.934
20	96.4		
36	82.0		
50	83.1		
65	73.7		

Table A5.24 – Methanol Removal in MBR, Temperature 70 °C, April 2, 1998

Time (min)	Methanol (mg/L)	Co	124.4
		K	0.36
5	122.3	I^2	0.957
20	114.1		
36	113.1		
51	103.9		
65	96.8		

Table A5.25 – Methanol Removal in MBR, Temperature 70 °C, April 3, 1998

Time (min)	Methanol (mg/L)	Co	161.4
		K	0.35
5	156.8	I^2	0.915
20	155.6		
36	149.9		
50	137.5		
65	135.1		

Table A5.26 – Methanol Removal in MBR, Temperature 70 °C, April 4, 1998

Time (min)	Methanol (mg/L)	Co	179.5
		K	0.27
5	177.0	I^2	0.935
20	173.3		
36	170.1		
50	159.9		
65	158.7		

Table A5.27 – Methanol Removal in MBR, Temperature 70 °C, April 10, 1998

Time (min)	Methanol (mg/L)	Co	510.0
		K	0.28
5	502.7	I^2	0.710
20	499.4		
36	501.1		
50	492.2		
65	470.1		

Table A5.28 – Methanol Removal in MBR, Temperature 70 °C, April 13, 1998

Time (min)	Methanol (mg/L)	Co	434.8
		K	0.15
6	433.8	I^2	0.991
20	427.6		
35	422.6		
50	419.0		
65	413.8		

Table A5.29 – Methanol Removal in MBR, Temperature 70 °C, April 14, 1998

Time (min)	Methanol (mg/L)	Co	441.2
		K	0.13
5	441.7	I^2	0.928
20	434.6		
35	427.9		
50	425.7		
65	423.6		

Table A5.30 – Methanol Removal in MBR, Temperature 70 °C, April 20, 1998

Time (min)	Methanol (mg/L)	Co	445.4
		K	0.0098
5	0.0	I^2	0.885
20	441.6		
35	433.2		
50	431.8		
65	428.5		

Table A5.31 – Methanol Removal in MBR, Temperature 70 °C, April 23, 1998

Time (min)	Methanol (mg/L)	Co	432.5
		K	0.063
5	433.5	I^2	0.744
20	426.2		
35	424.5		
50	416.3		
65	421.0		

Table A5.32 – Methanol Removal in MBR, Temperature 70 °C, April 30, 1998

Time (min)	Methanol (mg/L)	Co	443.4
		K	0.16
5	439.6	I^2	0.948
20	438.7		
35	432.3		
50	427.9		
65	419.9		

Table A5.33 – Methanol Removal in MBR by Inactivated Biomass, Temperature 55 °C, May 15, 1998

Time (min)	Methanol (mg/L)	Co	97.8
		K1	0.00021
0	97.2	I^2	0.996
120	95.1		
480	89.5		
1260	75.5		
1350	73.2		

Table A5.34 – Methanol Removal in MBR by Inactivated Biomass, Temperature 55 °C, May 16, 1998

Time (min)	Methanol (mg/L)	Co	100.7
		K1	0.00020
0	101.2	I^2	0.993
120	98.5		
480	90.5		
1260	79.5		
1350	76.2		

Table A5.35 – Methanol Removal in MBR by Inactivated Biomass, Temperature 60 °C, May 18, 1998

Time (min)	Methanol (mg/L)	Co	103.3
		K1	0.00022
0	103.6	I^2	0.990
165	100.2		
360	94.8		
1200	79.1		
1560	74.1		

Table A5.36 – Methanol Removal in MBR by Inactivated Biomass, Temperature 60 °C, May 22, 1998

Time (min)	Methanol (mg/L)	Co	105.3
		K1	0.00026
0	105.6	I^2	0.993
165	100.5		
360	95.5		
1260	78.0		
1560	69.4		

Table A5.37 – Methanol Removal in MBR by Inactivated Biomass, Temperature 65 °C, May 24, 1998

Time (min)	Methanol (mg/L)	Co	103.7
		K1	0.00034
0	102.9	I^2	0.999
105	101.1		
435	89.3		
1485	62.6		
1530	62.0		

Table A5.38 – Methanol Removal in MBR by Inactivated Biomass, Temperature 65 °C, May 25, 1998

Time (min)	Methanol (mg/L)	Co	104.9
		K1	0.00031
0	104.5	I^2	0.995
105	100.2		
435	93.5		
1485	65.5		

Table A5.39 – Methanol Removal in MBR by Inactivated Biomass, Temperature 70 °C, May 28, 1998

Time (min)	Methanol (mg/L)	Co	101.3
		K1	0.00038
0	100.3	I^2	0.999
105	97.4		
435	87.0		
1225	63.3		
1360	59.8		

Table A5.40 – Methanol Removal in MBR by Inactivated Biomass, Temperature 70 °C, May 29, 1998

Time (min)	Methanol (mg/L)	Co	103.4
		K1	0.00042
0	103.2	I^2	0.994
105	97.5		
435	87.5		
1225	63.5		
1485	54.1		

Table A5.41 – Summary of Observed Growth Yield Calculations

(Operating Temperature of 55 °C)

(measured values in bold)

Date	Cumulative Time	Co (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm (Total) (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
10-Jan-98	0	**82.5**	**3.4**	**20.8**	20.5	**1.14**	0.61	665	**2672**	400	0	0
12-Jan-98	2	85.6	**3.5**	22.7	19.3	1.14	0.65	690	2512	400	11034	-550
13-Jan-98	3	**85.6**	**4.0**	22.7	22.0	**1.14**	0.65	691	**2512**	**400**	16562	454
15-Jan-98	5	**84.4**	**3.8**	22.7	20.6	**1.12**	0.61	681	2632	400	27452	4480
16-Jan-98	6	96.6	3.8	**22.7**	20.6	1.28	0.69	779	2632	400	33684	5533
17-Jan-98	7	96.6	3.8	22.7	20.6	1.28	0.69	779	2632	400	39916	6586
18-Jan-98	8	97.8	**3.8**	22.7	20.6	1.19	0.65	788	2632	**400**	46221	7638
19-Jan-98	9	97.8	3.8	**22.7**	20.6	1.19	0.65	788	**2632**	380	52526	8639
20-Jan-98	10	**96.6**	3.8	22.7	20.6	**1.28**	0.72	779	2556	380	58685	8365
28-Jan-98	18	**97.8**	**3.8**	22.7	20.6	**1.19**	0.66	788	**2556**	**380**	109273	17380
											Yield	**0.16**

Table A5.42 – Summary of Observed Growth Yield Calculations

(Operating Temperature of 60 °C)

(measured values in bold)

Date	Cumulative Time	Co (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm (Total) (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
4-Feb-98	0	**106**	**3.7**	**8.8**	51.9	**1.06**	0.63	861	2368	**417**	0	0
8-Feb-98	4	109	**3.8**	7.7	61.3	1.44	0.86	893	**2368**	**425**	28566	4026
10-Feb-98	6	**109**	**3.9**	**7.7**	62.9	**1.44**	0.82	894	2480	**420**	42866	7901
12-Feb-98	8	108	3.8	7.7	62.6	1.42	0.81	885	2480	383	57031	9802
14-Feb-98	10	108	**3.8**	7.7	62.6	1.42	0.81	885	2480	**383**	71196	11703
16-Feb-98	12	108	3.8	7.7	62.6	1.42	0.81	885	2480	**433**	85361	13853
17-Feb-98	13	**108**	3.8	**7.7**	62.6	**1.42**	0.81	885	**2480**	410	92443	14870
21-Feb-98	17	94	3.8	13.7	34.9	1.26	0.74	763	2416	410	116844	16784
22-Feb-98	18	**94**	3.8	13.7	34.9	**1.26**	0.74	763	2416	410	122944	17774
25-Feb-98	21	**109**	3.8	13.7	34.9	**1.43**	0.84	884	2416	410	144159	20746
27-Feb-98	23	104	**3.8**	13.7	34.9	1.37	0.80	843	**2416**	**410**	157654	22727
28-Feb-98	24	**104**	3.8	**13.7**	34.9	**1.37**	0.80	843	2416	410	164402	23718
											Yield	**0.14**

Table A5.43 – Summary of Observed Growth Yield Calculations

(Operating Temperature of 65 °C)

(measured values in bold)

Date	Cumulative Time	Co (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm (Total) (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
5-Mar-98	0	**136**	4.0	**12.5**	40.0	**0.56**	0.39	763	1976	410	0	0
6-Mar-98	1	**211**	**4.0**	12.8	39.2	**0.62**	0.43	850	1976	**410**	6797	810
8-Mar-98	3	157	**3.5**	12.8	34.3	0.64	0.44	878	1976	440	20851	2549
10-Mar-98	5	157	**4.3**	12.8	41.7	0.64	0.44	878	**1976**	**440**	34906	4288
12-Mar-98	7	**157**	3.5	12.8	34.3	**0.64**	0.47	878	1858	410	48960	3923
17-Mar-98	12	**160**	3.5	12.8	34.3	**0.68**	0.50	936	**1858**	410	86400	7732
19-Mar-98	14	157	**3.5**	12.8	34.3	0.58	0.41	792	1948	**410**	99072	10770
24-Mar-98	19	**157**	4.0	**12.8**	39.2	**0.58**	0.41	792	1948	**433**	130752	14987
30-Mar-98	25	**139**	**4.0**	12.8	39.2	**0.63**	0.44	864	**1948**	**433**	206784	24273
											Yield	**0.12**

Table A5.44 – Summary of Observed Growth Yield Calculations

(Operating Temperature of 70 °C)

(measured values in bold)

Date	Cumulative Time	Co (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm (Total) (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
10-Apr-98	0	**434**	**4.3**	**14.4**	37.6	**0.33**	0.41	418	1024	363	0	0
13-Apr-98	3	441	**3.5**	13.9	31.5	0.30	0.37	374	1024	**363**	8986	1114
14-Apr-98	4	**441**	**4.3**	**13.9**	38.3	**0.30**	0.37	374	**1024**	**375**	11981	1498
15-Apr-98	5	445	**4.0**	13.6	36.7	0.27	0.33	331	992	**380**	14630	1619
20-Apr-98	10	**445**	**4.0**	**13.6**	36.7	**0.27**	0.33	331	992	**367**	27878	3437
21-Apr-98	11	432	4.1	11.2	45.8	0.23	0.28	274	**992**	367	30067	3801
22-Apr-98	12	432	4.1	11.2	45.8	0.23	0.29	274	940	367	32256	3730
23-Apr-98	13	**432**	**4.1**	**11.2**	45.8	**0.23**	0.29	274	**940**	**367**	34445	4075
30-Apr-98	20	**443**	**3.9**	11.2	43.3	**0.29**	0.38	360	940	**375**	54605	6543
1-May-98	21	443	3.9	**11.2**	43.3	0.29	0.38	360	**940**	375	57485	6895
3-May-98	23	443	**3.9**	11.2	43.3	0.29	0.38	360	940	**385**	63245	7619
											Yield	**0.12**

A5.2 Part II – Effect of Rate of Temperature Increase, the Acclimatization Temperature and the Source of the Inoculum on Methanol Removal Kinetics

The daily volume of evaporator condensate treated, the ultrafiltration membrane flux, the concentration of MLVSS and the daily volume of sludge wasted, measured during Part II are presented in Tables A5.58 and A5.59.

The results from the investigation of the removal of methanol, monitored during Part II for selected batch feed cycles, are presented in Tables A5.45 to A5.56. For these tables, the parameter K corresponds to the zero order coefficient for the biological removal of methanol (mg/L•minute), as presented in Equation 4.4, the parameter Co corresponds to the methanol concentration in the MBR at the start of the selected batch feed cycle (mg/L) and the parameter Res_{TOC} corresponds to the residual TOC concentration present in the MBR at the end of the selected feed cycles (mg/L).

The R^2 value, presented in the following tables, is the correlation of determination for linear regression.

The observed growth yields, for the operating temperatures investigated, are presented in Tables A5.57 and A5.58.

The results from the tests using radio-labeled methanol are presented in Table A5.60.

Table A5.45 – Methanol Removal in MBR, Temperature 60 °C, November 3, 1998

Time (min)	Methanol (mg/L)		
		Co	123
		K	1.40
15	100.8	R^2	0.999
30	81.4	Res_{TOC} (mg/L)	12.0
45	59.5		
60	37.2		
75	17.0		

Table A5.46 – Methanol Removal in MBR, Temperature 60 °C, November 5, 1998

Time (min)	Methanol (mg/L)		
		Co	113
		K	1.42
15	89.8	R^2	0.997
30	70.4	Res_{TOC} (mg/L)	15.3
45	52.0		
60	26.3		
75	4.8		

Table A5.47 – Methanol Removal in MBR, Temperature 60 °C, November 12, 1998

Time (min)	Methanol (mg/L)		
		Co	113
		K	1.48
15	0.0	R^2	0.987
30	69.7	Res_{TOC} (mg/L)	13.2
45	44.1		
60	18.7		
75	3.7		

Table A5.48 – Methanol Removal in MBR, Temperature 60 °C, November 18, 1998

Time (min)	Methanol (mg/L)		
		Co	123
		K	1.36
15	99.5	R^2	0.975
30	83.0	Res_{TOC} (mg/L)	12.4
45	66.2		
60	36.1		

Table A5.49 – Methanol Removal in MBR, Temperature 62 °C, November 24, 1998

Time (min)	Methanol (mg/L)		
		Co	104
		K	1.16
15	86.1	R^2	0.999
30	68.0	Res_{TOC} (mg/L)	14.0
45	50.9		
60	33.0		
75	16.0		

Table A5.50 – Methanol Removal in MBR, Temperature 63 °C, November 30, 1998

Time (min)	Methanol (mg/L)		
		Co	107
		K	1.17
15	90.2	R^2	0.998
30	70.3	Res_{TOC} (mg/L)	11.6
45	52.1		
60	36.0		
75	19.0		

Table A5.51 – Methanol Removal in MBR, Temperature 65 °C, December 8, 1998

Time (min)	Methanol (mg/L)		
		Co	111
		K	1.21
15	92.2	R^2	1.000
30	73.5	Res_{TOC} (mg/L)	14.4
45	54.6		
60	36.5		
75	19.0		

Table A5.52 – Methanol Removal in MBR, Temperature 65 °C, December 17, 1998

Time (min)	Methanol (mg/L)		
		Co	109
		K	0.85
15	95.9	R^2	0.996
30	81.5	Res_{TOC} (mg/L)	11.8
45	71.7		
60	55.2		
75	43.8		

Table A5.53 – Methanol Removal in MBR, Temperature 65 °C, December 20, 1998

Time (min)	Methanol (mg/L)	Co	104
		K	0.78
15	92.6	R^2	0.989
30	80.8	Res_{TOC} (mg/L)	13.0
45	64.2		
60	56.2		
75	42.4		
90	33.0		

Table A5.54 – Methanol Removal in MBR, Temperature 65 °C, December 28, 1998

Time (min)	Methanol (mg/L)	Co	111.4
		K	0.86
15	97.3	R^2	1.000
30	85.4	Res_{TOC} (mg/L)	10.3
45	71.6		
60	58.9		
75	45.5		
90	31.6		

Table A5.55 – Methanol Removal in MBR, Temperature 65 °C, January 3, 1999

Time (min)	Methanol (mg/L)	Co	112
		K	0.80
15	99.2	R^2	1.000
30	87.7	Res_{TOC} (mg/L)	13.6
45	73.8		
60	61.5		
75	48.9		
90	38.6		

Table A5.56 – Methanol Removal in MBR, Temperature 65 °C, January 6, 1999

Time (min)	Methanol (mg/L)	Co	110
		K	0.74
15	101.7	R^2	0.989
30	83.5	Res_{TOC} (mg/L)	12.1
45	75.1		
60	62.9		
75	52.5		
90	42.2		

Table A5.57 – Methanol Removal in MBR, Temperature 65 °C, January 12, 1999

Time (min)	Methanol (mg/L)	Co	108
		K	0.73
15	98.4	R^2	0.992
30	83.3	Res_{TOC} (mg/L)	14.8
45	70.7		
60	61.9		
75	52.7		
90	39.5		

Table A5.58 – Summary of Observed Growth Yield Calculations

(Operating Temperature of 60 °C - Part II)

(measured values in bold)

Date	Operating Temp. (oC)	Cumulative Time (days)	Co Real (mg/L)	Co alculated mg/l	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm Total (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
26-Oct-98	60	0	123	113	**3.9**	9.4	51.3	1.42	0.83	1002	**2424**	**400**	0	0
29-Oct-98	60	3	123	113	**3.8**	9.4	51.1	1.42	0.83	1001	2424	400	24033	2909
30-Oct-98	60	4	123	113	3.8	9.4	51.1	1.42	0.83	1001	**2424**	400	32044	3878
2-Nov-98	60	7	123	111	**3.8**	9.4	50.0	1.42	0.69	1001	2924	**357**	56060	19011
3-Nov-98	60	8	**123**	111	3.8	**9.4**	50.0	**1.42**	0.69	1001	2924	357	64065	20056
5-Nov-98	60	10	**113**	109	**3.7**	**9.4**	49.3	**1.44**	0.88	920	**2317**	**400**	78792	12197
6-Nov-98	60	11	113	109	3.7	9.4	49.3	1.50	0.78	921	2717	400	86161	16484
9-Nov-98	60	14	113	118	**4.0**	9.4	53.7	1.50	0.86	924	**2492**	400	108343	14074
10-Nov-98	60	15	113	118	4.0	9.4	53.7	1.50	0.85	924	2496	400	115737	15105
12-Nov-98	60	17	**113**	116	**3.9**	**9.1**	54.1	**1.50**	0.85	924	2496	**371**	130520	16959
13-Nov-98	60	18	123	116	3.9	9.1	54.1	1.38	0.78	1002	2496	371	138539	17886
18-Nov-98	60	23	**123**	116	3.9	9.1	54.1	**1.38**	0.78	1002	**2496**	371	178632	22521
													Yield	0.13

Table A5.59 – Summary of Observed Growth Yield Calculations

(Operating Temperature of 65 °C - Part II)

(measured values in bold)

Date	Operating Temp. (oC)	Cumulative Time (days)	Co Real (mg/L)	Co alculated mg/l	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm Total (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
18-Nov-98	61	-	104	118	**4.0**	17.6	28.3	1.16	0.66	840	**2496**	370		
20-Nov-98	61	-	104	118	**4.0**	17.6	28.3	1.16	0.64	840	2568	**370**		
22-Nov-98	62	-	104	90	3.0	17.6	21.3	1.16	0.64	837	2568	367		
23-Nov-98	62	-	104	90	**3.0**	17.6	21.3	1.16	0.64	837	2568	**367**		
24-Nov-98	62	-	**104**	116	4.0	**17.6**	28.0	**1.16**	0.64	840	**2568**	360		
25-Nov-98	62	-	107	116	**4.0**	20.8	23.7	1.17	0.69	863	2388	**360**		
26-Nov-98	63	-	107	118	**4.0**	20.8	24.0	1.17	0.69	863	2388	465		
30-Nov-98	64	-	**107**	114	**3.9**	**20.8**	23.3	**1.17**	0.69	863	**2388**	**465**		
2-Dec-98	64	-	111	118	**4.0**	18.3	27.3	1.21	0.75	896	2284	**360**	0	0
4-Dec-98	65	0	111	116	**4.0**	18.3	27.0	1.21	0.74	896	**2284**	360	28674	3289
7-Dec-98	65	3	111	118	**4.0**	18.3	27.3	1.21	0.77	896	2192	**360**	35844	3448
8-Dec-98	65	4	**111**	115	3.9	**18.3**	26.7	**1.21**	0.77	896	2192	393	43011	4309
9-Dec-98	65	5	109	115	**3.9**	17.0	28.6	0.85	0.54	878	2192	**393**	64081	5169
12-Dec-98	65	8	109	116	**3.9**	17.0	28.8	0.85	0.54	878	2192	**417**	71105	7909
13-Dec-98	65	9	109	113	3.8	17.0	28.1	0.85	0.54	878	**2192**	433	85149	8859
15-Dec-98	65	11	109	113	**3.8**	17.0	28.1	0.85	0.60	878	1956	**433**	99193	6778
17-Dec-98	65	13	**109**	118	4.0	**17.0**	29.3	**0.85**	0.60	878	1956	413	106219	8395
18-Dec-98	65	14	104	118	**4.0**	**16.9**	29.7	0.78	0.55	838	1956	**413**	119623	9204
20-Dec-98	65	16	**104**	69	**3.1**	**12.1**	32.0	**0.78**	0.55	837	**1956**	**432**	173181	10892
28-Dec-98	65	24	**111.4**	91	**4.1**	**12.9**	40.0	**0.86**	0.57	900	**2104**	**445**	209184	27854
2-Jan-99	65	29	102	88	**4.0**	14.3	35.0	0.80	0.57	823	1948	**417**	215768	25673
3-Jan-99	65	30	**112**	85	3.8	**14.3**	33.5	**0.80**	0.57	902	1948	433	222987	26515
4-Jan-99	65	31	110	85	3.8	15.0	31.9	0.74	0.52	886	**1948**	433	244243	27358
6-Jan-99	65	33	**110**	85	**3.8**	**15.0**	31.9	**0.74**	0.52	886	1948	**433**	265498	29885
7-Jan-99	65	34	108	85	3.8	15.0	31.9	0.73	0.52	870	**1925**	**433**	321150	31831
12-Jan-99	65	41	**108**	85	3.8	15.0	31.9	**0.73**	0.51	870	**1970**	433	321150	40055
													Yield	0.12

Table A5.60 – ^{14}C- Methanol Recoveries Measured During Batch Degradability Tests

Operating Temperature		55	Operating Temperature		60	Operating Temperature		65
Fraction of 14C-Methanol added recovered as		Fraction as biomass	Fraction of 14C-Methanol added recovered as		Fraction as biomass	Fraction of 14C-Methanol added recovered as		Fraction as biomass
Biomass	CO2	(A/(A+B))	Biomass	CO2	(A/(A+B))	Biomass	CO2	(A/(A+B))
(A)	(B)							
0.086	0.476	0.153	0.119	0.616	0.162	0.085	0.693	0.109
0.090	0.496	0.153	0.099	0.603	0.141	0.085	0.698	0.108
0.095	0.466	0.169	0.090	0.658	0.120	0.080	0.676	0.105
0.087	0.520	0.143	0.093	0.647	0.125	0.057	0.687	0.077
0.090	0.522	0.147	0.090	0.623	0.144	0.062	0.669	0.084
0.092	0.502	0.154	0.085	0.562	0.131	0.058	0.705	0.076
0.090	0.497	0.153				0.071	0.688	0.094
0.067	0.460	0.127				0.065	0.610	0.096
0.064	0.448	0.125				0.063	0.670	0.086
0.064	0.444	0.125				0.060	0.589	0.092
0.073	0.459	0.138				0.064	0.638	0.091
0.063	0.478	0.116				0.066	0.656	0.092
0.068	0.481	0.123				0.059	0.553	0.096
0.064	0.449	0.125				0.063	0.619	0.092
0.068	0.442	0.133						
0.066	0.458	0.127						
Average		0.138			0.137			0.093
+/- 90%		0.025			0.025			0.017

Appendix 6 – Data Collected During Experiment Investigating the Effect of the Evaporator Condensate Matrix on the Biological Removal of Methanol

Appendix 6 contains the data collected during Parts I, II and III, of the experiment investigating the effects of the contaminant matrix present in evaporator condensate, presented in Chapter 6. Appendix 6 also contains data collected during the experiment investigating the removal of non-methanolic organic contaminants, presented in Chapter 7.

A6.1 Part I - Identification of Potential Effects of the Real Evaporator Condensate Matrix on the Specific Methanol Utilization Rate

The daily volume of evaporator condensate treated, the ultrafiltration membrane flux, the concentration of MLVSS and the daily volume of sludge wasted, measured during Part II are presented in Tables A6.21 and A6.23.

The results from the investigation of the effects of the contaminant matrix on methanol removal, monitored during Part I for selected batch feed cycles, are presented in Tables A6.1 to A6.19. For these tables, the parameter K corresponds to the zero order coefficient for the biological removal of methanol (mg/L•minute), as presented in Equation 4.4, and the parameter Co corresponds to the methanol concentration in the MBR at the start of the selected batch feed cycle (mg/L). In Tables A6.1 to A6.4, the parameter K' corresponds to the zero order coefficient for the removal of TOC (mg/L•minute). In Tables A6.11 to A6.19, the parameter K' corresponds to the first order coefficient for the removal of TOC (/minute), as presented in Equation 7,6. The parameter So corresponds to the TOC concentration in the MBR at the start of the selected batch feed cycle (mg/L) and Sp corresponds to the residual TOC concentration in the MBR at the end of the selected batch feed cycle (mg/L).

The results from the investigation of the abiotic removal of methanol and TOC, monitored during Part I using inactivated biomass, are presented in Table A6.20. In this table, the parameters K and K' corresponds to the first order coefficients for the stripping of methanol (/minute) and TOC (/minute) as presented in Equations 4.2 and 7.1, respectively.

The R^2 value, presented in the following tables, is the coefficient of determination for linear regression. Similarly, the I^2 value is the correlation index square for non-linear regression.

The parameters K'' and R^{2}', in Tables A6.11 to A6.19, are for two sequential zero order relationships fitted to the TOC concentrations in the MBR, as discussed in Section 7.3.1. The parameter K'' corresponds to the zero order coefficient for the first sequential zero order function (mg/L•minute) and the parameter R^{2}' corresponds to the coefficient of determination for the two sequential zero order relationships fitted to the TOC concentrations in the MBR.

The observed growth yield for the different feed compositions investigated is presented in Tables A6.21 to A6.23.

Table A6.1– Methanol Removal in MBR, 0 % Real Condensate, October 14, 1998

Time (min)	Methanol (mg/L)	TOC (mg/L)
15	85.3	38.3
30	71.5	31.9
45	53.5	27.1
60	36.9	23.2
75	12.1	17.1
90	0.0	14.6
105	0.0	14.7
120	0.0	
175	0.0	13.4

Methanol	
Co	111.0
K	1.30
R^2	0.992
TOC	
So	47.9
Sp	14.2
K'	0.34
R^2	0.994

Table A6.2 – Methanol Removal in MBR, 0 % Real Condensate, October 26, 1998

Time (min)	Methanol (mg/L)	TOC (mg/L)
15	84.6	32.0
30	66.8	27.0
45	45.9	22.0
60	26.0	20.0
75	8.5	16.0
90	0.0	13.0
105	0.0	
120	0.0	14.0
0	0.0	

Methanol	
Co	104.3
K	1.28
R^2	0.999
TOC	
So	35.1
Sp	13.5
K'	0.26
R^2	0.980

Table A6.3 – Methanol Removal in MBR, 0 % Real Condensate, November 3, 1998

Time (min)	Methanol (mg/L)	TOC (mg/L)
15	81.6	31.1
30	66.0	24.4
45	47.0	21.8
60	21.1	15.3
75	5.8	14.0
90	0.0	7.7
105	0.0	7.4
120	0.0	7.5
175	0.0	10.7

Methanol	
Co	103.3
K	1.31
R^2	0.993
TOC	
So	34.3
Sp	8.3
K'	0.29
R^2	0.960

Table A6.4 – Methanol Removal in MBR, 0 % Real Condensate, November 9, 1998

Time (min)	Methanol (mg/L)	TOC (mg/L)
15	79.7	31.4
30	60.1	25.6
45	40.1	18.3
60	22.1	13.3
75	0.3	9.3
90	0.0	7.5
105	0.0	8.2
120	0.0	7.6
175	0.0	7.8

Methanol	
Co	99.7
K	1.32
R^2	0.999
TOC	
So	36.5
Sp	7.8
K'	0.37
R^2	0.989

Table A6.5 – Methanol Removal in MBR, 10 % Real Condensate, November 30, 1998

Time (min)	Methanol (mg/L)
15	89.5
30	67.6
45	45.0
60	23.6
75	3.9
90	0.0
105	0.0
120	0.0
175	0.0

Co	109.3
K	1.42
R^2	0.999

Table A6.6 – Methanol Removal in MBR, 10 % Real Condensate, December 8, 1998

Time (min)	Methanol (mg/L)
15	91.1
30	71.2
45	52.8
60	36.4
75	14.4
90	0.0
105	0.0
120	0.0
175	0.0

Co	109.6
K	1.25
R^2	0.998

Table A6.7 – Methanol Removal in MBR, 10 % Real Condensate, December 18, 1998

Time (min)	Methanol (mg/L)		
15	81.4	Co	99.3
30	63.9	K	1.21
45	44.2	R^2	0.993
60	22.7		
75	11.0		
90	0.0		
105	0.0		
120	0.0		
175	0.0		

Table A6.8 – Methanol Removal in MBR, 10 % Real Condensate, December 29, 1998

Time (min)	Methanol (mg/L)		
15	75.7	Co	95.9
30	57.2	K	1.32
45	35.3	R^2	0.999
60	16.8		
75	0.4		
90	0.0		
105	0.0		
120	0.0		
175	0.0		

Table A6.9 – Methanol Removal in MBR, 10 % Real Condensate, January 7, 1999

Time (min)	Methanol (mg/L)		
15	82.7	Co	97.2
30	58.0	K	1.13
45	48.9	R^2	0.985
60	30.4		
75	11.9		
90	0.0		
105	0.0		
120	0.0		
175	0.0		

Table A6.10 – Methanol Removal in MBR, 10 % Real Condensate, January 11, 1999

Time (min)	Methanol (mg/L)		
15	69.2	Co	86.4
30	50.5	K	1.17
45	33.7	R^2	1.000
60	16.1		
75	0.0		
90	0.0		
105	0.0		
120	0.0		
175	0.0		

Table A6.11 – Methanol Removal in MBR, 100 % Real Condensate, January 14, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
15	81.1	73.5	Co	95.3
30	71.6	66.0	K	0.83
45	61.2	59.8	R^2	0.987
60	43.2	57.6	TOC	
75	33.1	52.9	So	87.0
90	0.0	51.5	Sp	52.1
105	0.0	65.3	K'	1.13
120	0.0	45.3	I^2	0.769
175	0.0		K''	0.33
			$R^{2,}$	0.636

Table A6.12 – Methanol Removal in MBR, 100 % Real Condensate, January 18, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
15	67.2	69.5	Co	81.1
30	54.6		K	0.88
45	43.1	58.7	R^2	0.998
60	28.8	54.1	TOC	
75	14.3	51.5	So	82.9
90	0.0	48.6	Sp	46.92
105	0.0	49.4	K'	.90
120	0.0		I^2	0.951
175	0.0	49.2	K''	0.31
			$R^{2,}$	0.683

Table A6.13 – Methanol Removal in MBR, 100 % Real Condensate, January 22, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
			Co	101
15	90.8	88.8	K	0.77
30	77.6	80.9	R^2	0.999
45	66.5	75.8	TOC	
60	55.9	68.1	So	101.9
75	44.3	65.1	Sp	52.18
90		61.8	K'	.93
105			I^2	0.961
120		52.4	K''	0.40
175		57.2	$R^{2'}$	0.656

Table A6.14 – Methanol Removal in MBR, 100 % Real Condensate, January 25, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
			Co	104.9
15	94.3	85.6	K	0.76
30	81.2	78.0	R^2	0.999
45		73.0	TOC	
60	58.8	66.0	So	99.3
75	48.4	62.0	Sp	58.4
90		63.0	K'	1.07
105			I^2	0.982
120		58.0	K''	0.39
175		61.0	$R^{2'}$	0.640

Table A6.15 – Methanol Removal in MBR, 100 % Real Condensate, February 4, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
			Co	100.5
15	84.6	83.0	K	0.97
30	70.9	75.0	R^2	0.966
45		73.0	TOC	
60	49.2	63.2	So	94.9
75	23.0	61.0	Sp	51.9
90		57.6	K'	0.87
105	0.0		I^2	0.982
120		56.1	K''	0.37
175		54.6	$R^{2'}$	0.963

Table A6.16 – Methanol Removal in MBR, 100 % Real Condensate, February 9, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
			Co	93.7
15		75.6	K	0.91
30	67.0	70.2	R^2	0.999
45	52.3	61.3	TOC	
60	38.4	59.9	So	88.9
75	24.4	55.9	Sp	51.32
90	12.4	54.4	K'	1.00
105	0.0		I^2	0.984
120		51.0	K''	0.35
175		53.4	$R^{2'}$	0.606

Table A6.17 – Methanol Removal in MBR, 100 % Real Condensate, February 12, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
			Co	93.7
15		75.9	K	0.90
30	67.1	72.6	R^2	0.999
45		59.2	TOC	
60	38.7	61.9	So	87.9
75	25.5	56.2	Sp	50.9
90	13.1	53.0	K'	.92
105	0.0	0.0	I^2	0.954
120		53.4	K''	0.33
175		52.1	$R^{2'}$	0.761

Table A6.18 – Methanol Removal in MBR, 100 % Real Condensate, February 21, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
			Co	85.0
15	67.8	83.3	K	0.90
30	61.6	77.8	R^2	0.990
50	45.2	70.2	TOC	
60	29.7	67.5	So	95.9
75	16.8	60.9	Sp	55.76
90	3.4	58.7	K'	.91
105	0.0		I^2	0.979
120		60.6	K''	0.37
175		56.5	$R^{2'}$	0.784

Table A6.19 – Methanol Removal in MBR, 100 % Real Condensate, February 24, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
15	73.3	84.3	Co	85.0
30	54.6	77.2	K	0.88
50	39.1	72.9	R^2	0.989
60	30.5	68.6	TOC	
75	18.2	58.5	So	97.7
90	4.1	57.1	Sp	52.2
105	0.0		K'	0.93
120		54.6	I^2	0.955
175		56.2	K''	0.40
			$R^{2'}$	0.720

Table A6.20– Methanol Removal in MBR, 100 % Real Condensate, Inactivated Biomass, February 25, 1999

Time (min)	Methanol (mg/L)	TOC (mg/L)	Methanol	
15	73.9	98.0	Co	73.1
30	72.7	97.3	K	0.00025
45	72.2	94.6	R^2	0.754
60	71.5	95.4	TOC	
75	71.8	92.6	So	100.0
90	70.1	93.5	Sp	90.7
120	71.6	91.9	K'	.014
180	69.6	92.8	I^2	0.871
240	69.5	90.0		

Table A6.21 – Summary of Observed Growth Yield Calculations

(0 % Real Evaporator Condensate in Feed)

(measured values in bold)

Date	Cumulative Time (days)	Co Real (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm Total (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
9-Oct-98	0	111	**4.0**	**12.5**	40.0	1.30	0.87	901	2150	**400**	0	0
13-Oct	4	111	**3.9**	11.2	43.8	1.30	0.87	902	2150	**403**	28863	3462
14-Oct	5	**111**	3.9	11.2	43.8	**1.30**	0.87	902	2150	403	36079	4327
15-Oct-98	6	104	3.9	11.2	43.8	1.28	0.86	848	2150	403	42864	5192
16-Oct-98	7	104	**3.9**	11.2	43.6	1.28	0.86	848	2150	**400**	49648	6052
19-Oct-98	10	104	**4.3**	11.2	48.4	1.28	0.86	851	2150	**410**	70076	8697
22-Oct-98	13	104	**4.1**	11.2	45.4	1.28	0.86	849	2150	**407**	90457	11320
26-Oct-98	17	**104**	**4.3**	**11.2**	47.5	**1.28**	0.86	851	**2150**	**400**	117674	14760
29-Oct-98	20	103	**4.2**	11.4	45.7	1.32	0.94	842	2030	400	137884	14316
30-Oct-98	21	103	4.2	11.4	45.7	1.32	0.94	842	**2030**	400	144621	15128
2-Nov-98	24	103	**4.2**	11.4	46.3	1.32	0.89	843	2125	**397**	164842	19940
3-Nov-98	25	**103**	4.2	11.4	46.3	**1.31**	0.89	842	2125	**397**	171582	20783
4-Nov-98	26	100	4.2	11.4	46.3	1.32	0.89	814	2125	**397**	178092	21627
5-Nov-98	27	100	**3.9**	11.4	43.1	1.32	0.89	812	2125	**400**	184584	22477
6-Nov-98	28	100	3.9	11.4	43.1	1.32	0.89	812	**2125**	**400**	191077	23327
9-Nov-98	31	**100**	3.9	**11.4**	43.1	**1.32**	0.87	812	**2190**	**400**	210556	27515
12-Nov-98	34	100	**3.9**	11.4	43.1	1.32	0.87	812	2190	**386**	230034	30050
13-Nov-98	35	100	**4.0**	11.4	43.9	1.32	0.87	812	2190	**400**	236530	30926
											Yield	0.13

Table A6.22 – Summary of Observed Growth Yield Calculations
(10 % Real Evaporator Condensate in Feed)
(measured values in bold)

Date	Cumulative Time (days)	Co Real (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm Total (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
26-Nov-98	1	109	**1.5**	3.2	58.3	1.42	0.97	202	2108	80	0	0
30-Nov-98	5	**109**	**1.1**	**3.2**	43.7	**1.42**	0.97	199	**2108**	**80**	6365	675
2-Dec-98	7	110	**1.2**	3.2	47.6	1.25	0.90	200	2010	81	9560	650
4-Dec-98	9	110	**1.3**	3.2	48.5	1.25	0.90	200	2010	81	12757	974
7-Dec-98	12	110	**1.2**	3.2	47.9	1.25	0.90	200	**2010**	**81**	17550	1460
8-Dec-98	13	**110**	1.1	**3.0**	44.2	**1.25**	0.90	199	2010	81	19139	1622
9-Dec-98	14	99	**1.1**	18.8	7.0	1.21	0.85	177	2045	**74**	20554	1835
12-Dec-98	17	99	**1.0**	18.8	6.7	1.21	0.85	177	2045	**92**	24795	2398
14-Dec-98	19	99	1.2	**18.8**	7.8	1.21	0.85	177	2045	102	27626	2816
15-Dec-98	20	99	**1.2**	17.0	8.6	1.21	0.85	177	2045	**102**	29041	3026
18-Dec-98	23	**99**	**1.2**	**17.0**	8.7	**1.21**	0.85	229	**2045**	**87**	34538	3559
21-Dec-98	26	96	**1.2**	**17.4**	8.7	1.32	0.86	236	**2220**	**96**	40203	5131
24-Dec-98	29	96	**1.2**	**17.6**	8.7	1.32	0.85	238	**2235**	**102**	45914	5897
28-Dec-98	33	96	**1.2**	15.3	10.0	1.32	0.87	238	2195	**94**	53523	6438
29-Dec-98	34	**96**	1.2	**15.3**	10.0	**1.32**	0.87	238	**2195**	86	55426	6626
30-Dec-98	35	97	**1.2**	12.9	11.8	1.13	0.73	238	2210	**86**	57327	6843
4-Jan-99	40	97	1.3	**12.9**	12.2	1.13	0.73	246	**2210**	**82**	67156	7747
6-Jan-99	42	97	1.3	12.9	12.2	1.13	0.71	246	2285	77	71088	8366
7-Jan-99	43	**97**	**1.3**	**12.9**	12.2	**1.13**	0.71	246	**2285**	**77**	76986	8894
11-Jan-99	47	**86**	**1.3**	**11.7**	13.5	**1.17**	0.72	248	**2345**	**84**	84909	10112
											Yield	0.12

Table A6.23 – Summary of Observed Growth Yield Calculations

(100 % Real Evaporator Condensate in Feed)

(measured values in bold)

Date	Cumulative Time (days)	Co Real (mg/L)	Influent Volume (L/day)	Flux (mL/min)	Time of Filter Eff (min)	Rm Total (mg/L.min)	Usu (/d)	MeOH Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mL/d)	Cumulative MeOH (mg)	Cumulative Solids (mg)
12-Jan-99	0	95	0.7	12.5	7.2	0.83	0.55	170	2175	85	0	0
14-Jan-99	2	**95**	**0.7**	**12.5**	7.2	**0.83**	0.55	170	**2175**	**85**	2721	370
18-Jan-99	6	**81**	**2.3**	**13.5**	21.5	**0.88**	0.59	147	**2140**	**106**	7423	1030
21-Jan-99	9	81	**2.0**	15.3	16.5	0.77	0.53	146	**2095**	**102**	10922	1429
22-Jan-99	10	**101**	2.4	**15.3**	19.4	**0.77**	0.52	183	2128	116	12383	1733
25-Jan-99	13	**105**	**2.4**	**15.5**	19.2	**0.76**	0.51	189	**2128**	**116**	16917	2471
29-Jan-99	17	101	**2.4**	15.5	19.5	0.97	0.66	182	2128	**102**	22733	3337
1-Feb-99	20	101	**2.4**	**14.6**	20.3	0.97	0.62	182	**2255**	**103**	27096	4714
4-Feb-99	23	**101**	**2.3**	**15.3**	18.4	**0.97**	0.57	181	**2440**	**100**	31450	6431
9-Feb-99	28	**94**	**2.3**	**13.6**	20.6	**0.91**	0.54	169	2440	**98**	38227	7632
11-Feb-99	30	94	2.3	13.6	20.6	0.90	0.54	169	**2404**	98	40937	7977
12-Feb-99	31	**94**	**2.4**	**13.6**	22.0	**0.90**	0.54	170	2404	**94**	42295	8204
14-Feb-99	33	85	**2.5**	10.9	28.5	0.90	0.54	155	2404	**111**	44779	8737
17-Feb-99	36	85	**2.3**	10.9	26.1	0.90	0.54	155	**2405**	**104**	48490	9495
20-Feb-99	39	85	**2.4**	10.9	28.1	0.90	0.52	155	2495	**96**	52214	10695
21-Feb-99	40	**85**	2.4	10.9	27.0	**0.90**	0.52	155	2495	89	53453	10917
22-Feb-99	41	85	**2.4**	**10.9**	27.0	0.88	0.51	155	**2495**	**89**	54691	11139
24-Feb-99	43	**85**	**2.3**	**10.0**	28.1	**0.88**	0.51	155	2495	**93**	57167	11600
											Yield	0.20

A6.2 Part II: Identification of the Potential Direct Inhibitory Effect of Real Evaporator Condensate Matrix on a Mixed Microbial Culture Acclimatized to Synthetic Evaporator Condensate

The results from the experiment investigating of the potential direct inhibitory effect of the contaminant matrix on condensate matrix on a mixed microbial culture acclimatized to synthetic evaporator condensate, measured during Part II using off-line degradability tests, are presented in Tables A6.24 to A6.38. For these tables, the parameter K corresponds to the zero order coefficient for the biological removal of methanol (mg/L•minute), as presented in Equation 4.4, and the parameter Co corresponds to the methanol concentration in the MBR at the start of the selected batch feed cycle (mg/L).

The results from the investigation of the abiotic removal of methanol, monitored during Part II using inactivated biomass, are presented in Tables A6.37 and A6.38. In these tables, the parameter K corresponds to the first order coefficient for the stripping of methanol (/minute) as presented in Equation 4.2.

The R^2 value, presented in the following tables, is the coefficient of determination for linear regression. Similarly, the I^2 value is the correlation index square for non-linear regression.

Table A6.24 – Methanol Removal in Off-Line Batch Test, 0 % Real Condensate, October 19, 1998

Time (min)	Methanol (mg/L)	Co	74.8
		K	0.68
5	71.3	R^2	0.999
20	60.6		
35	51.7		
50	41.0		
65	29.9		

Table A6.25 – Methanol Removal in Off-Line Batch Test, 0 % Real Condensate, October 26, 1998

Time (min)	Methanol (mg/L)	Co	77.4
		K	0.83
5	72.5	R^2	0.995
20	61.8		
35	49.5		
50	33.8		
65	24.5		

Table A6.26 – Methanol Removal in Off-Line Batch Test, 0 % Real Condensate, October 28, 1998

Time (min)	Methanol (mg/L)	Co	75.8
		K	0.72
5	70.8	R^2	0.995
20	63.4		
35			
50	40.4		
65	28.6		

Table A6.27 – Methanol Removal in Off-Line Batch Test, 10 % Real Condensate, October 19, 1998

Time (min)	Methanol (mg/L)	Co	72.1
		K	0.67
5	68.3	R^2	0.999
20	58.9		
35	49.2		
50	38.2		
65	28.2		

Table A6.28 – Methanol Removal in Off-Line Batch Test, 10 % Real Condensate, October 20, 1998

Time (min)	Methanol (mg/L)	Co	75.4
		K	0.72
5	71.9	R^2	0.998
20	61.5		
35	49.0		
50	40.2		
65	28.5		

Table A6.29 – Methanol Removal in Off-Line Batch Test, 10 % Real Condensate, October 26, 1998

Time (min)	Methanol (mg/L)	Co	65.8
		K	0.60
5	62.0	R^2	0.998
20	54.8		
35	44.9		
50	35.8		
65	26.3		

Table A6.30 – Methanol Removal in Off-Line Batch Test, 60 % Real Condensate, October 21, 1998

Time (min)	Methanol (mg/L)	Co	66.2
		K	0.62
5	63.7	R^2	0.999
20	53.1		
35	44.8		
50	35.4		
65	26.4		

Table A6.31 – Methanol Removal in Off-Line Batch Test, 60 % Real Condensate, October 26, 1998

Time (min)	Methanol (mg/L)	Co	64.9
		K	0.65
5	62.9	R^2	0.979
20	49.0		
35	42.4		
50	35.1		
65	20.7		

Table A6.32 – Methanol Removal in Off-Line Batch Test, 60 % Real Condensate, October 29, 1998

Time (min)	Methanol (mg/L)	Co	66.1
		K	0.73
5	65.6	R^2	0.966
20	46.2		
35	42.0		
50	30.9		
65	18.7		

Table A6.33 – Methanol Removal in Off-Line Batch Test, 100 % Real Condensate, November 8, 1998

Time (min)	Methanol (mg/L)	Co	67.1
		K	0.73
5	61.1	R^2	0.983
20	55.5		
35	40.6		
50	32.0		
65	17.8		

Table A6.34 – Methanol Removal in Off-Line Batch Test, 100 % Real Condensate, October 30, 1998

Time (min)	Methanol (mg/L)	Co	66.3
		K	0.82
5	64.2	R^2	0.992
20	46.9		
35	37.5		
50	25.6		
65	13.0		

Table A6.35 – Methanol Removal in Off-Line Batch Test, 100 % Real Condensate (Concentrated Solids), November 3, 1998

Time (min)	Methanol (mg/L)	Co	84.9
		K	0.68
5	83.4	R^2	0.988
20	68.5		
35	61.8		
50	50.9		
65	41.5		

Table A6.36 – Methanol Removal in Off-Line Batch Test, 100 % Real Condensate (Concentrated Solids), November 9, 1998

Time (min)	Methanol (mg/L)	Co	85.1
		K	0.60
5	81.8	R^2	0.997
20	72.9		
35	65.2		
50	56.0		
65	45.6		

Table A6.37 – Abiotic Methanol Removal in Off-Line Batch Test, 100 % Real Condensate, October 19, 1998

Time (min)	Methanol (mg/L)	Co	74.9
		K	0.0005
5	74.7	I^2	0.583
20	74.6		
35	72.2		
50	74.1		
65	73.0		
80	71.5		

Table A6.38 – Abiotic Methanol Removal in Off-Line Batch Test, 100 % Real Condensate, November 3, 1998

Time (min)	Methanol (mg/L)	Co	71.4
		K	0.0004
5	72.9	I^2	0.157
20	76.7		
35	70.7		
50	72.2		
65	72.8		
80	71.9		

A6.3 Part III: Effect of Non-Methanolic Substances, Present in Real Evaporator Condensate Matrix, on the Composition of the Microbial Community Present in the MBR

The results from the experiment investigating the effect of non-methanolic substances on the microbial community, measured during Part III using off-line degradability tests with radio-labeled methanol are presented in Table A6.39. Results for the experiment investigating 0% real evaporator condensate in the feed (100 % synthetic evaporator condensate) are presented in Table A5-60.

Table A6.49 – ^{14}C- Methanol Recoveries Measured During Batch Degradability Tests

10% Real Condensate in Feed			100 % Real Condensate in Feed		
Fraction of 14C-Methanol Added recovered as		Fraction as Biomass	Fraction of 14C-Methanol added recovered as		Fraction as biomass
Biomass (A)	CO_2 (B)	(A/(A+B))	Biomass (A)	CO_2 (B)	(A/(A+B))
0.1584046	0.877192	0.15296	0.0694698	0.591867	0.105045
0.1165125	0.857298	0.119646	0.0773851	0.559662	0.121475
0.1046413	0.811442	0.114227	0.0548848	0.553784	0.090172
0.0941906	0.526986	0.151633	0.0746128	0.615344	0.108141
0.1584046	0.877192	0.15296	0.0439159	0.578543	0.070552
0.1046413	0.811442	0.114227	0.0476525	0.616519	0.071747
			0.0613202	0.585953	0.094736
			0.0578045	0.591648	0.089005
			0.0649132	0.632067	0.093135
			0.0659608	0.576465	0.102675
			0.0570189	0.646095	0.081095
			0.0516312	0.609853	0.078054
			0.0514068	0.561962	0.083811
			0.0581226	0.603015	0.087913
Average		0.134275			0.091254
+/- 90%		0.032942			0.023609

Appendix 7 – Data Collected During Experiment Investigating the Fate of Reduced Sulphur Compounds During Treatment

Appendix 7 contains the experimental data collected during the RSC mass balance done on the MBR, presented in Chapter 7 and Appendix A1.4.

The results of the RSC mass balance done on the MBR, under normal and abiotic operating conditions, are presented in Tables A7.1 to A7.3 and Tables A7.4 and A7.5, respectively. The results collected when synthetic condensate was used as feed are presented in Tables A7.6 and A7.7.

Table A7.1 - Biotic Mass-Balance Test with Real Condensate, February 19, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0min	12.7	5.7	31.2	14.0	16.8	7.5	4.1	1.8
t= 5 min Caustic	1.0	0.0	9.8	0.2	2.7	0.1	1.3	0.0
t= 15 min Caustic	6.5	0.2	60.3	1.5	9.0	0.2	5.7	0.1
t=30 min Caustic	0.0	0.0	7.4	0.2	3.9	0.1	44.6	1.1
t=45 min Caustic	0.0	0.0	1.8	0.0	1.1	0.0	36.2	0.9
t=60 min Caustic	0.0	0.0	2.6	0.1	0.3	0.0	8.3	0.2
t=20 min Ethanol	0.0	0.0	20.7	0.5	91.8	2.3	22.0	0.6
t=40 min Ethanol	0.0	0.0	10.0	0.3	47.5	1.2	30.8	0.8
t=60 min Ethanol	0.0	0.0	3.8	0.1	42.5	1.1	20.2	0.5
MBR t=60 min	0.0	0.0	0.0	0.0	0.7	1.3	0.4	0.7
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.2		2.9		5.0		4.2
Removed		5.7		14.0		6.3		1.1
%		3.3		20.8		79.3		377.9

Table A7.2 - Biotic Mass-Balance Test with Real Condensate, February 19, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0min	13.1	5.9	33.2	14.9	18.4	8.2	5.1	2.3
t= 5 min Caustic	1.4	0.0	15.1	0.4	2.6	0.1	1.3	0.0
t= 15 min Caustic	3.7	0.1	54.6	1.4	10.4	0.3	9.5	0.2
t=30 min Caustic	0.0	0.0	3.4	0.1	3.1	0.1	69.6	1.7
t=45 min Caustic	0.0	0.0	1.2	0.0	1.1	0.0	41.9	1.0
t=60 min Caustic	0.0	0.0	2.4	0.1	0.0	0.0	8.8	0.2
t=20 min Ethanol	0.0	0.0	33.1	0.8	89.2	2.2	21.9	0.5
t=40 min Ethanol	0.0	0.0	15.1	0.4	70.7	1.8	33.9	0.8
t=60 min Ethanol	0.0	0.0	3.3	0.1	53.7	1.3	41.6	1.0
MBR t=60 min	0.0	0.0	0.0	0.0	0.5	0.9	0.3	0.5
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.1		3.2		5.8		5.7
Removed		5.9		14.9		7.3		1.7
%		2.2		21.6		78.6		327.3

Table A7.3 - Abiotic Mass-Balance Test with Real Condensate, February 25, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0mir	12.9	5.8	33.2	14.9	20.1	9.0	3.8	1.7
t= 5 min Caustic	1.8	0.0	10.1	0.3	2.8	0.1	1.2	0.0
t= 15 min Caustic	8.2	0.2	58.5	1.5	8.8	0.2	5.9	0.1
t=30 min Caustic	0.0	0.0	8.2	0.2	3.9	0.1	48.8	1.2
t=45 min Caustic	0.0	0.0	1.8	0.0	1.1	0.0	34.9	0.9
t=60 min Caustic	0.0	0.0	2.6	0.1	0.3	0.0	10.3	0.3
t=20 min Ethanol	0.0	0.0	19.1	0.5	99.4	2.5	18.2	0.5
t=40 min Ethanol	0.0	0.0	9.2	0.2	73.6	1.8	26.4	0.7
t=60 min Ethanol	0.0	0.0	3.5	0.1	53.3	1.3	27.2	0.7
MBR t=60 min	0.0	0.0	0.0	0.0	0.6	1.1	0.3	0.5
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.3		2.8		6.1		4.3
Removed		5.8		14.9		7.9		1.2
%		4.3		19.0		76.8		371.5

Table A7.4 - Abiotic Mass-Balance Test with Real Condensate, February 25, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0min	12.9	5.8	30.5	13.6	18.4	8.2	4.4	2.0
t= 5 min Caustic	1.4	0.0	11.7	0.3	2.6	0.1	1.3	0.0
t= 15 min Caustic	6.1	0.2	57.8	1.4	9.3	0.2	7.0	0.2
t=30 min Caustic	0.0	0.0	6.3	0.2	3.6	0.1	45.3	1.1
t=45 min Caustic	0.0	0.0	1.6	0.0	1.1	0.0	32.1	0.8
t=60 min Caustic	0.0	0.0	2.5	0.1	0.2	0.0	9.1	0.2
t=20 min Ethanol	0.0	0.0	19.4	0.5	90.5	2.3	22.0	0.6
t=40 min Ethanol	0.0	0.0	11.0	0.3	46.5	1.2	33.4	0.8
t=60 min Ethanol	0.0	0.0	3.8	0.1	41.9	1.0	30.6	0.8
MBR t=60 min	0.0	0.0	0.0	0.0	0.7	1.3	0.4	0.7
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.2		2.9		4.9		4.5
Removed		5.8		13.6		7.0		1.3
%		3.2		20.9		70.1		360.7

Table A7.5 - Abiotic Mass-Balance Test with Real Condensate, February 26, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0min	11.4	5.1	34.5	15.4	21.2	9.5	4.8	2.1
t= 5 min Caustic	1.0	0.0	13.8	0.3	3.1	0.1	1.2	0.0
t= 15 min Caustic	4.7	0.1	54.5	1.4	9.9	0.2	6.9	0.2
t=30 min Caustic	0.0	0.0	5.4	0.1	3.3	0.1	64.4	1.6
t=45 min Caustic	0.0	0.0	1.8	0.0	1.0	0.0	34.9	0.9
t=60 min Caustic	0.0	0.0	2.0	0.1	0.4	0.0	10.2	0.3
t=20 min Ethanol	0.0	0.0	33.1	0.8	88.7	2.2	21.9	0.5
t=40 min Ethanol	0.0	0.0	15.0	0.4	79.1	2.0	33.9	0.8
t=60 min Ethanol	0.0	0.0	3.5	0.1	56.0	1.4	41.6	1.0
MBR t=60 min	0.0	0.0	0.0	0.0	0.8	1.4	0.3	0.5
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.1		3.2		6.0		5.4
Removed		5.1		15.4		8.1		1.6
%		2.8		20.9		75.0		333.6

Table A7.6 - Mass-Balance Test with Synthetic Condensate, February 20, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0min	0.0	0.0	0.0	0.0	13.1	5.9	8.8	3.9
t= 5 min Caustic	0.0	0.0	0.0	0.0	2.6	0.1	1.8	0.0
t= 15 min Caustic	0.0	0.0	0.0	0.0	8.6	0.2	5.5	0.1
t=30 min Caustic	0.0	0.0	0.0	0.0	2.6	0.1	4.1	0.1
t=45 min Caustic	0.0	0.0	0.0	0.0	0.9	0.0	0.8	0.0
t=60 min Caustic	0.0	0.0	0.0	0.0	0.3	0.0	0.4	0.0
t=20 min Ethanol	0.0	0.0	0.0	0.0	58.1	1.5	28.0	0.7
t=40 min Ethanol	0.0	0.0	0.0	0.0	44.5	1.1	27.3	0.7
t=60 min Ethanol	0.0	0.0	0.0	0.0	33.7	0.8	23.8	0.6
MBR t=60 min	0.0	0.0	0.0	0.0	0.5	0.8	0.6	1.1
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.0		0.0		3.8		2.3
Removed		0.0		0.0		5.1		2.8
%		0.0		0.0		74.8		81.0

Table A7.7 - Mass-Balance Test with Synthetic Condensate, February 20, 1999

	H2S		CH3SH		DMS		DMDS	
	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR	mg/L	mg in MBR
inf. to MBR at t=0min	0.0	0.0	0.0	0.0	12.9	5.8	9.8	4.4
t= 5 min Caustic	0.0	0.0	0.0	0.0	2.5	0.1	1.1	0.1
t= 15 min Caustic	0.0	0.0	0.0	0.0	7.6	0.2	13.9	0.4
t=30 min Caustic	0.0	0.0	0.0	0.0	2.5	0.1	4.6	0.1
t=45 min Caustic	0.0	0.0	0.0	0.0	0.8	0.0	0.3	0.0
t=60 min Caustic	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0
t=20 min Ethanol	0.0	0.0	0.0	0.0	53.9	1.3	24.4	0.6
t=40 min Ethanol	0.0	0.0	0.0	0.0	39.2	1.0	28.9	0.7
t=60 min Ethanol	0.0	0.0	0.0	0.0	25.1	0.6	25.5	0.6
MBR t=60 min	0.0	0.0	0.0	0.0	0.4	0.8	0.7	1.3
MBR t=180 min	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Recovered		0.0		0.0		3.4		2.6
Removed		0.0		0.0		5.0		3.1
%		0.0		0.0		67.5		84.0

Appendix 8 – Cost Estimates for a Full-Scale High Temperature MBR for the Treatment of Evaporator Condensate for Reuse

The cost estimates presented in Chapter 8 are summarized below.

A8.1 Membrane Bioreactor

Reactor Tank

The quote for the reactor tank component of the MBR was obtained from Dennerik Engineering, Burnaby, Canada. The quote includes the following.

- 300 m^3 tank (see Section 8.3)
  - 316 stainless steel tank
    - 3.5 m radius
    - 10 m high
    - access cover on surface
    - miscellaneous nozzles and fittings
  - Shipped to site and field erected

Budget price: $175,000

Ultrafiltration System

a) Ceramic ultrafiltration system

The quote for the ceramic ultrafiltration system was obtained from US Filters, Warrendale, PA, USA. The quote includes the following.

- Skid mounted package system (delivered and installed)

- ceramic tubular ultrafiltration membrane (500 angstrom pore size)
  - 223 m^2 of membrane surface (see Section 8.3)
  - 24 modules in a 4 x 6 array
  - footprint 2.5m x 11m x 3m high
- recycling pump to provide 5 m/s over the membrane surface
- clean-in-place system
- process logic control
- Power requirement 118 KW

Budget Price: $833,000 (US) – Canadian equivalent of $1,300,000
Estimated operating cost: $0.35/ADMT

b) Polymeric ultrafiltration system

The quote for the polymeric ultrafiltration system was obtained from a membrane supplier based on the design parameters listed in Table 8.1. The design calculations were not available since they were considered to be propitiatory information. The supplier also requested anonymity. The quote includes the following.

- Package membrane system (delivered and installed)
  - Polymeric hollow fiber ultrafiltration membranes
  - Permeate handling system and negative pressure pumps (5-10 psi)
  - Backwash pumps and clean-in-place system
  - Blowers for coarse aeration system (to minimize membrane fouling)
    - 640 cfm air
    - 2% OTE
  - Power requirements 21 KW

Budget price: $600,000
Estimated power costs: $0.06/ADMT

Aeration System

The cost for the aeration system was estimated based on discussions with Dillon Consulting Ltd, London, Ontario, Canada. The aeration system is capable of providing 32 m^3/minute of air to the MBR (see Section 8.3). The cost estimate includes the following.

- variable frequency drive blowers (including blower silencers and controllers)
- ceramic diffusers (including header and connector piping)
- control system (including dissolved oxygen probes, and automated control valves)
- power supply and housing for aeration system components
- power requirements for aeration were estimated using Equation 10-13a from Metcalf and Eddy (1991). Based on a 10 m deep basin and a 90 % blower efficiency, the power required to supply 32 m^3/minute of air was estimated to be 39 kW.
- components delivered and installed

Estimated capital cost: $1,100,000
Estimated operating cost: $0.12/ADMT

Chemical Costs

The capital cost for the chemical addition system was estimated based on discussions with Dillon Consulting Ltd, London, Ontario, Canada. The capital cost estimate was based on the capital cost for a chemical addition system recently installed at an industrial wastewater treatment plant. The chemical addition system controlled both the pH and nutrient addition. The exact nutrient requirements were not determined in this study. Additional research would be required to estimate the optimal nutrient requirements. The operating costs associated with chemical addition for nutrient addition and pH control were adapted from Barton et al. (1996) based on the BOD removal in an aerobic membrane bioreactor. Costs were determined for the removal of 100 % of the influent methanol, as BOD. To account for the BOD contributed by non-methanolic compounds,

the BOD load, based on the influent methanol concentration, was increased by 30 %. The cost estimate includes the following.

- chemical storage tank
- solution make-up pumps and mixers
- solution storage tanks
- chemical addition pumps
- process logic control
- operating cost of $202 /day (cost of $0.097 /kg BOD removed, adapted from Barton et al. (1996) and a BOD load of 2082 kg/day)
- components delivered and installed

Estimated capital cost: $65,000
Estimated operating cost: $0.25/ADMT

Other Costs

Commissioning, engineering, contingency, contractor profit, administrative, legal and insurance costs are included in the above cost estimates. Costs for civil and electrical hook-up were estimated based on discussions with Dillon Consulting Ltd.

Additional civil and electrical costs: $660,000

A8.2 Steam Stripping System

The cost for the steam stripping system was obtained from three independent steam stripping suppliers. The equipment suppliers requested ananymity.

The quotes include the following.

- Steam stripping package (delivered and installed)
  - condensate pre-heater
  - stripping column
  - condenser
  - flame arresters
  - all pumps and valves
  - process logic control

Quote from supplier 1: $4,600,000
Quote from supplier 2: $5,000,000
Quote from supplier 3: $3,100,000

Based on discussions with consulting firms from Vancouver, the third quote was rejected since it was considered to be too low. The average quote from suppliers 1 and 2 was assumed as the cost for a steam stripping system to treat evaporator condensate.

The cost associated with steam generation is highly mill specific and is function of existing steam generating capacity. Based on discussions with engineering consulting firms from Vancouver, the cost of providing steam was estimated based on a life cycle cost for a large boiler, fired with gas and wood waste fuel, over a 20 year period. Given local conditions and 9 % financing, the life cycle cost of providing steam is estimated to be $5/1000 lb ($11/1000 kg) steam. This corresponds to a steam cost of $693,791 per year for an evaporator condensate flow of 0.6 m^3/minute.

The stripped condensate that is sent to the lime kiln for incineration has a heat value. The heat value of the stripped methanol was estimated to be 22,700 kJ/kg of methanol. Based on a 90 % methanol removal efficiency, an influent methanol concentration of 1236 mg/L and an evaporator condensate flow rate of 0.6 m^3/min, the heat value of methanol was

estimated to be 24,241,421 kJ/day. At a cost of $3.5/GJ, this corresponds to $84.84/day (CANMET, 1994).

Estimated capital cost: $4,800,000

Estimated power cost: $2.32/ADMT

Estimated fuel economy: $0.10/ADMT

Appendix 9 – Membrane Performance

The membrane component of the MBR consisted of a bench scale ceramic tubular ultrafiltration membrane as described in Chapter 3. The set-points for the different membrane operating parameters were determined based on discussions with the membrane supplier as presented in Chapter 3.

The effect of the set points for the different membrane operating parameters, on the membrane performance, were not investigated during the present study. However, the permeate flux was monitored. It was possible to consistently maintain a pseudo-steady state permeate flux of approximately 162 L/hour•m^2. A permeate flux of 162 L/hour•m^2 is typical for ultrafiltration membranes in MBR applications (personal communication, Johnson H., 1999, US Filters, USA). The measured permeate fluxes are presented in Tables A5.41 to A5.44 and A5.58 to A5.59, for experiment 2, presented in Chapter 5, and Tables A6.21 to A6.23, for experiments 3 and 4, presented in Chapters 6 and 7, respectively.

The permeate flux through the membrane component of the MBR decreased with time. When treating synthetic evaporator condensate, the decline in the permeate flux occurred relatively slowly. Membrane runs typically lasted 2 to 3 months before the permeate flux decreased to a point where the membrane had to be cleaned. Cleaning was performed as described below based on the recommendations of the membrane supplier. The cleaning procedure typically took approximately 2 hours. Approximately 100 % of the initial permeate flux was recovered following membrane cleaning.

When treating real evaporator condensate, the decline in the permeate flux occurred at a faster rate. Membrane runs typically lasted 4 to 6 weeks. However, only a fraction of the initial permeate flux could be recovered by using the cleaning procedure recommended by the membrane supplier (described below). Based on discussions with the membrane supplier, a new cleaning procedure was devised. This new cleaning procedure used a 40

% caustic solution. Approximately 100 % of the initial permeate flux was recovered following membrane cleaning with the stronger caustic solution. The nature of the increase in the rate of decline in the permeate flux was not investigated. Further studies are required to determine the cause of the higher rate of decline in the permeate flux when treating real evaporator condensate.

Filter Cleaning Procedure

1. Close permeate port to set cross-membrane pressure to 0 atmospheres.
2. Pump clean tap water through membrane for approximately 10 minutes.
3. Pump a NaOCl solution (200 to 300 mg/L) through membrane for approximately 10 minutes.
4. Pump clean tap water through membrane for 1 minute.
5. Pump a 2 % NaOH caustic solution through the membrane for 30 minutes.
6. Open permeate port and pump the caustic solution through the membrane for another 30 minutes.
7. Pump clean tap water through membrane until pH of the permeate is neutral (approximately 15 minutes).
8. Close permeate port.
9. Pump a 2 % HNO_3 acid solution through the membrane for 30 minutes.
10. Open permeate port and pump the acid solution through the membrane for another 20 minutes.
11. Pump clean tap water through membrane until pH of the permeate is neutral (approximately 15 minutes).