

**High Temperature Membrane Bioreactor Treating Kraft
Evaporator Condensate Under Steady and Transient Conditions**

by

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ABSTRACT

Research results from Bérubé (2000) have shown that the treatment of kraft evaporator condensate for reuse using a high temperature membrane bioreactor (MBR) is not only technically feasible, but can also be economically attractive. However, dynamics in daily operating conditions at kraft mills would result in non-steady state loadings to such a treatment system. Hence, the influence of transient operating conditions on an MBR system requires investigation before the system could be considered for full-scale plants.

Two bench-scale, high temperature MBRs (called R1 for Reactor 1 and R2 for Reactor 2) were operated under conditions proposed by Bérubé (2000) to examine system performance under steady state operation. The operating parameters selected were as follows - 38-day sludge retention time (SRT), 9-hr hydraulic retention time (HRT), and evaporator condensate that contained 1,200 mg methanol /L.

During the steady state experiment, the MBRs exhibited stable removal of the main contaminants. Removal efficiencies of 95 % for methanol and 64 % for organic components expressed as total organic carbon (TOC) were observed. Observed growth yields as low as 0.037 for R1 and 0.025 for R2 were found.

Effects of methanol shock loadings, black liquor spills, and pulp mill shutdown on a high temperature MBR treating condensate were the focus of the present research project. The reactors were subjected to four shock loadings to investigate long-term effects, and one shock loading to identify short-term effects.

Results showed that the high temperature MBRs were reasonably stable and able to achieve the same removal efficiency when the load was increased by 1.5 and 2 times instantaneously. Overload of methanol was observed during the methanol shock loading test with 2.5 times the regular methanol concentration. However, the system recovered 4 hours after the short-term shock loadings, and two days after the long-term shock loadings.

The MBRs started to show inhibitory effects after the long-term black liquor carryover test with 8 mL black liquor per litre condensate. During the black liquor carryover test with 16 mL black liquor per litre condensate, methanol removal efficiency was greatly decreased and this negatively influenced TOC and chemical oxygen demand (COD) removal efficiencies. However, the system recovered 4 hours after the short-term shock loadings, and two days after the long-term shock loadings. During the tests, the colour of the MBR permeates remained relatively constant while the dissolved solids concentrations of the permeates increased slightly.

Methanol, TOC, and COD utilization coefficients decreased during the shutdown period. However, the MBR system recovered along with resumption of loading fairly well. The MBR was capable of handling the 10-day shutdown period and recovered in 4 days to full capacity. No deleterious effects from 10-day shutdown were observed.

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ABBREVIATIONS

ACGIH	American Conference of Government and Industrial Hygienists
BOD	Biochemical oxygen demand
BOD ₅	Biochemical oxygen demand (5 day)
CH ₃ SH	Methyl mercaptan
COD	Chemical oxygen demand
DMDS	Dimethyl disulfide
DMS	Dimethyl sulfide
DO	Dissolved oxygen
EPA	Environmental Protection Agency
FTOC	Filtered total organic compound
H ₂ S	Hydrogen sulfide
HAP	Hazardous air pollutant
HRT	Hydraulic retention time
MACT	Maximum achievable control technology
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
MLTSS	Mixed liquor total suspended solids
MLVSS	Mixed liquor volatile suspended solids
NCASI	National council of the Paper Industry for Air and Stream Improvement
RSC	Reduced sulphur compound
SRT	Sludge retention time
TDCS	Total dissolved and colloidal solids
TOC	Total organic carbon
TS	Total Solids
TVDCS	Total volatile dissolved and colloidal solids
TVS	Total volatile solids
VOC	Volatile organic compound

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Chapter 1 Introduction

1.1 Problem Definition

Under the driver of stricter regulations and public concern on environmental issues, the pulp and paper industry is looking for solutions to achieve the goal of zero effluent discharge with requirements as follows. First, the technology must be able to treat a large volume of selected waste stream and diminish the use of fresh water, and thus minimize the volume of liquid effluent. Second, the system has to be able to reduce air pollutant emissions to the ambient environment. Third, the treatment process should be cost-effective and be able to attain the required efficiency under various operating conditions. Fourth, reuse of the treated wastewater should not significantly decrease the quality of the pulp mill products. Therefore, reuse of selected process waters with separate treatment is considered as one of the solutions and has been practiced in many mills.

For kraft mills, condensate, the condensed vapours produced through the chemical recovery process, is one of the potential process waters for recycle and reuse. Kraft condensates are typically divided into foul condensate and clean condensate. Under current operation, kraft mills typically reuse the 30 to 50% of clean condensate and sewer the remaining portion to be treated in a combined mill effluent treatment system (NCASI, 1995). Some mills also steam strip foul condensate before treatment to minimize potential hazards to ambient air quality (NCASI, 1994a).

Steam stripping is the technology most commonly used to treat the foul condensate (NCASI 1994a). However, the associated high expense for energy encourages the industry to consider alternative technologies that can minimize the presence of organic and particulate material in the process water, maximize the energy recovery, and significantly reduce the cost (Farr *et al.*, 1993). Among the potential treatment technologies for kraft condensate, the high temperature aerobic membrane bioreactor (MBR) has been identified as one of the most promising novel technologies (Bérubé, 2000).

An MBR is a modified activated sludge system whose clarifier is replaced by an ultrafiltration membrane unit and thus is able to achieve a zero-suspended solids effluent. For treatment of kraft condensates, a high temperature MBR has the advantages of good effluent quality, compact footprint, good energy recovery, and potentially low operating cost. However, an industrial biological treatment system usually suffers from frequent and severe variations in influent, both by volume and organic loads. Therefore, it's important to investigate the performance under transient conditions that a high temperature MBR may face.

The present research project continues the research effort initiated by Bérubé (2000) at the University of British Columbia's Pulp and Paper Centre. It was aimed to examine further the performance of an MBR under steady and transient conditions while treating kraft evaporator condensate.

1.2 Outline of the Thesis

This thesis consists of six chapters. Background literature review related to treatment of kraft condensate, membrane bioreactor technology, and shock loading research, is discussed in the Chapter 2. Chapter 3 outlines the objective of the present research project. A complete description of the experimental program and methods is provided in Chapter 4. Chapter 5 presents a summary of the experimental results and discussions, while detailed results are provided in the Appendix. Conclusions and recommendations for further work are given in Chapter 6.

Chapter 2 Background and Literature Review

2.1 Kraft Condensates

Pulping refers to the process by which wood is reduced to fibrous material (Smook, 1992). Generally, pulping methods can be divided into mechanical, chemical, and semi-chemical methods. The kraft pulping process is a chemical process that cooks the wood chips in a solution of sodium hydroxide and sodium sulfide at elevated temperature and pressure, and it has been dominant in North America since the 1950s.

In the kraft pulping process, condensed vapours, referred to as condensate, are produced mainly from the digester and the evaporator. From the sources, kraft condensates are simply classified into digester condensate and evaporator condensate. According to the chemical content, condensates are typically also segregated into clean condensates and foul condensates. Clean condensates contain fewer volatile organic compounds (VOCs) and are typically clean enough to reuse without treatment. Foul condensates typically represent 30 % - 40 % of the total evaporator process condensate flow, but contain 80 % of the methanol and 98 % of the reduced sulphur compounds (RSCs) (Blackwell, 1979). In some literature, condensates fall into three levels depending on chemical oxygen demand (COD) content: fairly clean, medium strength, and contaminated. Average volume and COD concentrations of condensates are shown in Table 2.1 (Danielsson and Hakansson, 1996).

Table 2.1 Examples of Condensates from a Kraft Mill
(Adapted from Danielsson and Hakansson, 1996)

Fraction	Condensate (m ³ /ADT*)	COD (mg/L)
Fairly Clean	5.0	200-400
Medium strength	4.0	1,500-2,000
Contaminated	1.1	10,000-15,000

* ADT – air-dried tonne pulp

2.1.1 Sources of Kraft Condensates

The typical kraft pulping process and sources of condensate are illustrated in Figure 2.1. During the cooking process, white liquor, which contains sodium sulphide (Na₂S) and sodium hydroxide (NaOH), are mixed with wood chips in the digester to dissolve the lignin from individual wood fibers. VOCs released by the chemical oxidation reactions are condensed and form condensates in the turpentine decanter and blow tank, depending on the cooking methods (batch or continuous). The cooked pulp mixtures are subsequently divided into pulp and spent cooking liquor, referred to as weak black liquor. The pulp is further processed into various paper products. To recover the cooking chemicals to be reused, the weak black liquors are concentrated by evaporation and condensates are produced throughout the recovery process.

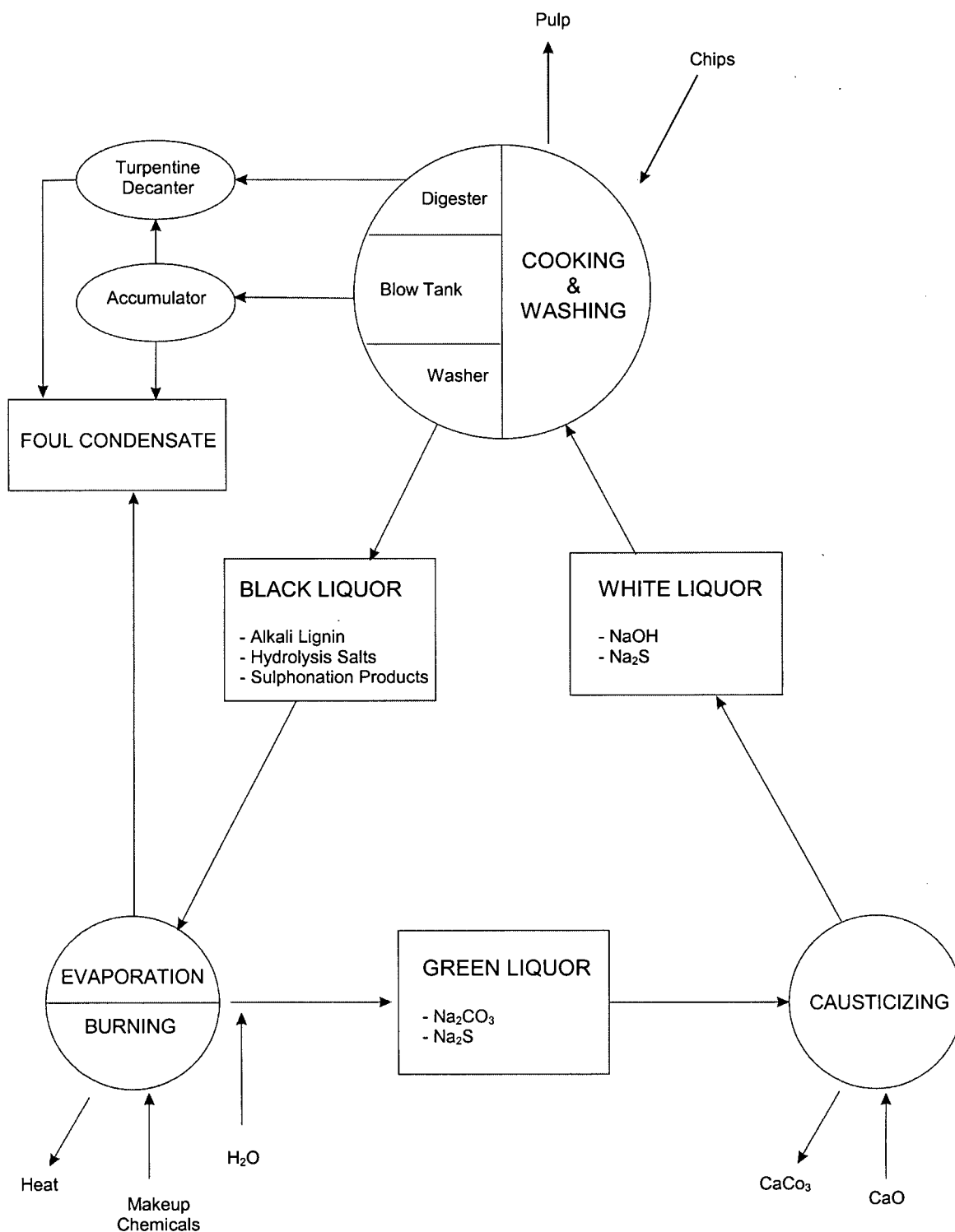


Figure 2.1 Typical Kraft Liquor Cycle and Sources of Kraft Condensates

(Adapted from Smook, 1992, and Mimms, 1993)

2.1.2 Characteristics of Kraft Condensates

Condensates are mainly water, but contain a number of volatile and semi-volatile compounds. Some non-volatile compounds, such as resin acids and salts, are present in the condensates usually as a result of physical entrainment of weak black liquor (Blackwell, 1979). Typical values for the concentrations of the main contaminants of concern are listed in Table 2.2.

Table 2.2 Typical Characteristics of the Kraft Condensates
(Adapted from Blackwell, 1979)

Compounds (mg/L)	Evaporator combined condensate	Batch Digester Condensate
Methanol	180-700	250-9100
Reduced Sulphur Compounds		
Hydrogen Sulphide (H ₂ S)	1-90	1-230
Methyl Mercaptan (CH ₃ SH)	1-30	40-340
Dimethyl Sulphide (DMS)	1-15	40-190
Dimethyl Disulphide (DMDS)	1-50	2-210
Total Organic Content (as BOD ₅)	60-1,100	720-9,200
Suspended Solids	30-70	
pH	9.2-9.6	6.0-11.1

Depending on the wood species, pulping process and equipment configuration (digester, evaporator, and the presence of turpentine recovery system), the characteristics of Kraft condensates vary. However, methanol and reduced sulphur compounds (RSCs) are always the main contaminants of concern of all.

Methanol (CH_3OH) contributes more than 80 % of the condensate BOD_5 and 95 % of the organic material (Blackwell, 1979; Hrutfiord *et al.*, 1973). One gram of methanol accounts for 1.5 g of chemical oxygen demand (COD) and approximately 1.1 g of biochemical oxygen demand (BOD) (Gay, 1974).

Hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulphide ($(\text{CH}_3)_2\text{S}$ or DMS), and dimethyl disulphide ($(\text{CH}_3)_2\text{S}_2$ or DMDS) are the four major volatile sulphur compounds in Kraft condensates. They are responsible for most of the strong odour and 75 % to 95 % of the toxicity of condensates (Environment Canada, 1979; Blackwell, 1979).

Other alcohols, ketones, small quantities of phenolic substances, and turpenes are the remainders. Turpenes are a problem in softwood cooking. They can represent a substantial portion of the condensate BOD if a turpentine recovery system is not used (NCASI, 1995).

2.2 Requirements and Regulations for Treatment of Kraft Condensates

2.2.1 Closed-cycle Concept in Pulp and Paper Industry

The closed-cycle concept was initially proposed by Rapson (1967). It refers to a pollution control practice that minimizes the liquid effluent by recycle and reuse of the process water. While a closed cycle mill minimizes the impact on the surrounding environment, it

also faces a number of challenges, including process operation and maintenance, product quality, and technical and economic feasibility. Increased heat content, contaminant concentrations, changes in pH and microbial growth in the process lines may result in a variety of detrimental process and product effects (Johnson *et al.*, 1996; Kotila and Estes, 1994). Therefore, research regarding closed cycle generation currently focuses on separation technology to remove trace contaminants from process water in order to reduce the effects of reusing process water on the pulp and paper industry.

2.2.2 Regulation Requirements

Ambient air quality in and around pulp and paper mills has gained increasing attention and has been controlled by standards recommended by the American Conference of Government and Industrial Hygienists (ACGIH, 1999). For the pulp and paper industry, methanol, H₂S, and CH₃SH concentrations should be lower than 200, 10 and 0.5 ppm respectively.

According to the Cluster Rule promulgated by the U.S. Environmental Protection Agency (EPA), air emissions and effluent discharges from the pulp and paper industry are under stricter control (Vice and Carroll, 1998). Based on the maximum achievable control technology (MACT), the Cluster Rule offers several alternatives for the control of kraft condensate listed below.

- Recycle condensates to a controlled process equipment.

- Steam stripping the condensates and destroy the hazardous air pollutants (HAPs) by incineration. Or other control devices can achieve the same requirement.
- Transport the condensate by a sealed pipe and a submerged inlet to a properly monitored combined mill effluent biological treatment system.

The steam stripping (or other devices) option has to achieve a removal efficiency that will result in: (1) removal of at least 92 % of the methanol (or total HAPs) by weight, (2) reduction of methanol (or total HAPs) to 330 mg/L for bleached mills and 210 mg/L for unbleached mills, (3) removal to 5.1 kg and 3.3 kg methanol (or total HAPs) per tonne of pulp produced for bleached mills and unbleached mills. For the option of treatment by the combined mill effluent biological treatment system, 82 % of methanol (or total HAPs) removal by weight has to be attained.

In addition, the “Clean Condensate Alternative” of the Cluster Rule offers the mills another option. To qualify for this alternative, a mill must demonstrate that the same level of methanol (or HAPs) reduction as described above will be achieved by reusing the condensate with pre-treatment. The baseline emissions, emission reductions, and test procedures are determined on a case-by-case basis.

Reusing the condensates under the Clean Condensate Alternative may require the methanol concentration in the treated condensate to be 20 mg/L based on rough estimation since it's site-specific (Barton *et al.*, 1998). The National Council of the Paper Industry for Air and Stream Improvement (NCASI, 1994a) recommends the

concentrations of methanol and suspended solids in the condensates should be less than 20 mg/L for reuse purpose.

2.3 Alternatives for Treatment of Kraft Condensates

Steam stripping, aerobic biological treatment, and anaerobic biological treatment are the three main methods investigated for treatment of Kraft condensates. The advantages and disadvantages of the three treatment methods are summarized in Table 2.3.

2.3.1 Steam Stripping

Steam stripping is the main technology currently used in the treatment of kraft condensate in North America (NCASI, 1994b). The efficiency of steam stripping on methanol removal depends on the steam to condensate ratio, condensate hydraulic retention time, and methanol transfer rate from the liquid phase to the vapour phase that is proportional to the methanol concentration in the condensate. However, the steam to condensate ratio and the associated cost increase significantly if more than a 75 % methanol removal efficiency is required (Zuncich *et al.*, 1993). In addition, steam stripping is less effective for methanol removal from clean to moderate strength condensate.

Table 2.3 Advantages and Disadvantages of Treatment Technologies for Kraft Condensate

Treatment Methods	Advantages	Disadvantages
Steam Stripping	<ul style="list-style-type: none"> • achieve 75 % methanol removal and 95 % of RSC removal by a steam to condensate ratio of 8 % by weight (McCance and Burke, 1980). • system performance is well understood at full-scale treatment of kraft condensate. • pre-cooling isn't required before treatment. • can use waste heat from the blow heat recovery system as an alternative steam source. (Farr <i>et al.</i>, 1993). 	<ul style="list-style-type: none"> • is not able to remove non- or semi-volatile contaminants or particulate material (Bérubé, 2000). • may need significant modifications to existing mill configuration (Farr <i>et al.</i>, 1993; NCASI 1994b). • cost increases significantly if more than 75 % of methanol removal efficiency is required. (NCASI 1994b). • 20 % of Kraft mills which use a steam stripper exceed the EPA methanol concentration limit (NCASI, 1994b).
Aerobic Biological Treatment	<ul style="list-style-type: none"> • achieve higher contaminant removal efficiencies. • potentially lower operating cost. • aeration of system is able to oxidize and strip RSCs. Emission can be minimized if designed as a closed system. 	<ul style="list-style-type: none"> • Pre-cooling is required for most of the systems. • generally higher solids content in the effluent and poor sludge settling characteristics at higher operating temperature (Barton <i>et al.</i>, 1998; Milet, 1998)
Anaerobic Biological Treatment	<ul style="list-style-type: none"> • moderate contaminant removal efficiencies. • potentially lower operating cost than aerobic biological system since aeration is not needed. 	<ul style="list-style-type: none"> • unstable removal efficiency and a long lag period after shutdown (Pipyn <i>et al.</i>, 1987; Qiu <i>et al.</i>, 1988). • may require pre-stripping to ensure stable performance (Pipyn <i>et al.</i>, 1987; Yamaguchi <i>et al.</i>, 1990) • limited information concerning the removal of RSCs. • varied solids concentrations in the effluent were observed in different systems and fluctuated with system performance (Barton <i>et al.</i>, 1998; Yamaguchi <i>et al.</i>, 1990; Qiu <i>et al.</i>, 1988).

2.3.2 Aerobic Biological Treatment

Aerobic biological treatment systems have been considered as a potential treatment method for kraft condensate. Barton *et al.* (1998) reported that higher methanol and COD removal efficiencies were observed in a completely mixed activated sludge system than in the anaerobic up-flow sludge blanket system, when the two systems were subjected to 0.88 BOD/g mixed-liquor volatile suspended solids (MLVSS) · day. However, higher RSC and trace HAP removal efficiencies reported in the aerobic system may be mostly due to stripping and abiotic oxidation (Milet, 1998; Mahmood *et al.*, 1999; Bérubé, 2000). Another main benefit of aerobic biological treatment systems is their resistance to toxic substances or shock loads, which is very beneficial to full-scale operation (Sierra-Alvarez *et al.*, 1994).

2.3.3 Anaerobic Biological Treatment

A number of anaerobic biological systems treating kraft condensate have been investigated. Up-flow sludge blanket system, fluidized bed system, fixed bed system, and suspended carrier system are the representative systems (Qiu *et al.*, 1998; Norman, 1983; Pipyn *et al.*, 1987; Yamaguchi *et al.*, 1990; Welander *et al.*, 1999). Generally, aerobic systems showed better contaminant removal efficiency than anaerobic systems.

2.4 Background of the Bioreactor used in this study

2.4.1 Membrane Bioreactor

The membrane bioreactor (MBR) was first developed in the 1970s (Smith *et al.*, 1969) because activated sludge systems often suffered from problems with poor sludge settlement and high solids contents in the effluent. Therefore, the clarifier in a conventional activated sludge system was replaced with an ultrafiltration membrane to improve liquid-solid separation.

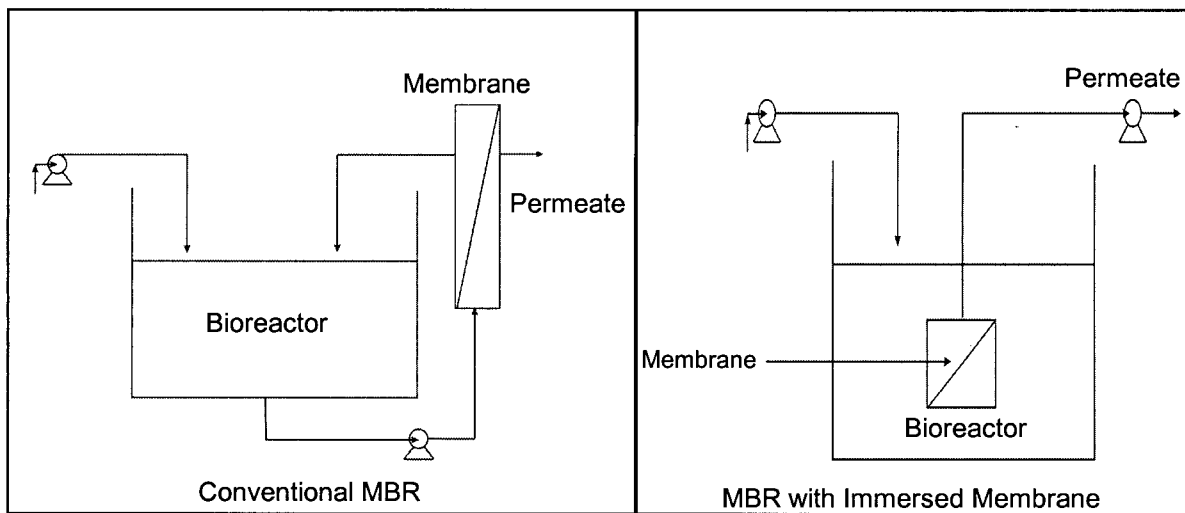


Figure 2.2 Configurations of Conventional MBR and MBR with Immersed Membrane

As presented in Figure 2.2, there are two general configurations of MBRs, conventional MBR or MBR with immersed membranes. Either approach has advantages and disadvantages, as shown Table 2.4. In a conventional MBR, mixed liquor is pumped to an external membrane unit at high velocities and trans-membrane pressures. In an MBR

with an immersed membrane, a vacuum pump is used to draw permeate from the membrane unit that is immersed in the reactor tank.

Table 2.4 Comparisons of Two Configurations of MBRs
(Adapted from Cho and *et al.*, 1999)

Characteristic	Conventional MBR	MBR with immersed membrane
Flux	Moderate	Low
Fouling Control	Less Difficult	Difficult
Energy use	High to low	Moderate
Retrofit	Easy	Less easy
Flexibility	Good	Limited

An MBR has a number of advantages over conventional aerobic biological treatment systems, summarized below.

- MBR achieves complete retention of biomass and suspended solids. As a result, very high biomass concentrations ranging from 10,000 to 30,000 mg MLVSS/L can be maintained in an MBR (Krauth and Staab, 1993; Dufresne *et al.*, 1998; Sato and Ishii, 1991; Magara and Itoh, 1991).
- High MLVSS concentration in a MBR allows the system to perform well under high organic loading rates. Therefore, a relatively small system size is needed. Moreover, the absence of the clarifier further reduces the footprint of an MBR required (Zaloum *et al.*, 1994; Thomas *et al.*, 2000).
- Separate control of the hydraulic retention time (HRT) and the sludge retention time (SRT) allows the system to be operated under better control to reduced sludge production and to achieve greater contaminant removal (Dufresne *et al.*, 1998; Trouve *et al.*, 1994).

- Retention of particulate and high molecular weight organics provides increased opportunity for biodegradation and good removal efficiency (Onysko, 1992).
- The high shear environment found in the recirculation line of the MBRs can lower the average particle size in the MBRs (Bailey *et al.*, 1994), and is believed to enhance the mass transfer to the biomass and improve the contaminant removal rate.
- An MBR is flexible to various operating parameters, such as high temperature and long SRT, without the need of concern for possible poor sludge settling (Onysko, 1992).
- Expansion or retrofit of the MBR system is relatively easy and flexible (Onysko, 1992).

However, a major concern with MBR technology is fouling control (Bérubé, 2000; Ragona, 1998). Under liquid-solid operation of a MBR, permeate (primary solute and dissolved materials) pass through the membrane, and rejected materials, including microorganisms and particulates, accumulate at the membrane surface as a “gel layer”. Since the layer increases the resistance to permeation, the permeate flux decreases as the thickness of the layer increases, and finally fouling of the membrane unit occurs (Sato and Ishii, 1991; Yamamoto *et al.*, 1989; Shimizu *et al.*, 1993; Rebsamen *et al.*, 1987).

Membrane type, operating conditions (trans-membrane pressure, crossflow velocity, turbulence, and etc.), and solution characteristics are the main factors affecting the rate of fouling (Fane, 1987). High MLVSS concentration in the MBR is considered to increase

the fouling problem since high solids concentration in the solution may result in higher rate of solids transfer from the solution to the membrane surface and further decrease the permeate flux (Magara and Itoh, 1991; Reismeier *et al.*, 1987). However, some research has indicated that the MLVSS concentration may have no effect on the permeate flux if turbulent conditions are maintained over a membrane surface (Lubbecke *et al.*, 1995; Ben Aim, 1999; Nagaoka *et al.*, 1996; Sato and Ishii, 1991; Magara and Itoh, 1991).

2.4.2 High Temperature Membrane Bioreactor Treating Kraft Condensates

The ability of aerobic biological treatment to treat kraft condensate has been proven (Milet, 1999; Bérubé, 2000). Among all the aerobic treatment systems, Bérubé (2000) suggested that high temperature MBR has the highest potential for treatment of kraft condensate for reuse. Over 99 % of the methanol and approximately 93 % of the organic contaminants contained in the influent evaporator condensate, measured as TOC were removed by a high temperature MBR during the experimental period. However, reduced sulphur compounds were removed mostly due to stripping (Milet, 1999; Bérubé, 2000).

From the experimental results, Bérubé (2000) suggested that the combined capital and operating costs for a high temperature MBR were estimated to be 40 % to 50 % less than those for a steam stripping system, while an MBR is capable of achieving a higher contaminant removal efficiency than a steam stripping system. This indicates that high temperature MBR is technically feasible, more effective, and more economical than steam stripping for the treatment of kraft condensate for reuse.

Aeration causes stripping of HAP and foul odorous compounds from the aerobic biological treatment system. An MBR can be designed as a closed system and emissions of HAP and temperature fluctuations can be minimized for system stability (Krauth and Staab, 1993).

2.4.3 Effects of High Temperature

The MBR used in the present study was operated at constant 60 °C. High temperature aerobic biological treatment is reported to have higher contaminant removal efficiencies and poor sludge settling ability (Allen and Tripathi, 1998; Flippin and Eckenfelder, 1994; LaPara and Alleman, 1999). However, the drawbacks of high temperature operation can be overcome by an MBR because of the complete retention of suspended solids. In addition, permeate flux increases at high temperature. Moreover, no cooling is required before treatment of kraft condensate and the heat content can be recovered because the temperature of kraft condensate typically ranges from 55 to 70 °C (Zuncich *et al.*, 1993).

Research has indicated that a combined effect of an increase of oxygen transfer coefficient and a decrease of oxygen saturation concentration with an increase of temperature resulted in a constant oxygen transfer rate regardless of the operating temperature (Vogelaar *et al.*, 2000; Bérubé, 2000).

Research has indicated that a combined effect of an increase of oxygen transfer coefficient and a decrease of oxygen saturation concentration with an increase of temperature resulted in a constant oxygen transfer rate regardless of the operating temperature (Vogelaar *et al.*, 2000; Bérubé, 2000).

2.4.4 Effects of Long Sludge Retention Time

From previous research, low surplus sludge production and low oxygen uptake rate have been observed for a biological treatment system with long sludge retention time (SRT) (Bérubé, 2000; Rosenberger *et al.*, 1999). Rosenberger *et al.* (1999) concluded that the MBR with a highly concentrated sludge is limited by organic carbon, not by oxygen. Nevertheless, it should be noticed that the increasing biomass concentration could influence the oxygen transfer rate of the system. Therefore, it is necessary to select high performance systems with adjustable energy input to maintain oxygen concentration in an MBR system (Wangner *et al.*, 1999).

Most MBRs are operated with partial removal of excess sludge. Recently, some researchers have reported that a zero surplus sludge production can be achieved by long, even infinite, SRT and F/M ratios as low as 0.1 kg COD / kg MLVSS · day (Rosenberger, 1999). However, the results published in the literature contradict each other (Chaize and Huyard, 1991; Canales *et al.*, 1994; Muller *et al.*, 1995) and further research needs to be done. An MBR without removal of excess sludge can largely reduce the costs of sludge disposal and is more economically attractive.

2.4.5 Transient Conditions

Dynamics in daily operating conditions at kraft mills result in non-steady state loadings to a wastewater treatment plant, with respect to volume, strength, and unexpected incidents such as spills. In addition, mill shutdowns may have deleterious effects on a biological treatment system. Therefore, the ability of a treatment system to cope with shock loads and mill shutdown is an important criterion for evaluating its suitability for full-scale implementation.

Rosenberger *et al.* (1999) concluded that no problems due to shock loading would be considered likely in a MBR that has a long SRT and a high biomass concentration. However, the influence of transient operating conditions on the system hasn't been fully investigated and further research is required prior to applying the system into full-scale plants.

Organic shock loads may be of at least two types: either a short-term transient that only lasts a few hours, or a longer-term change of days to weeks before reversion back to the original operating conditions. The microbial responses to short-term and long-term transients are expected to be identical in the first few hours to days; the biomass is expected to reach a new steady state after a long-term shock (Nachaiyasit and Stuckey, 1997a).

After discussions with Dr. Barton (Doug Barton, NCASI, 2001) and Ms. Taylor (Taylor J., 2001, Western Pulp Limited Partnership, Squamish, Canada), three scenarios for possible shock loads associated with treatment of kraft condensates are chosen to be investigated in this study. They are methanol shock loads, black liquor carryover, and mill shutdown.

Chapter 3 Objectives of the Research

Following Bérubé's research (2000), the main objective of the present study is to improve the understanding of performance of the high temperature MBR treating kraft evaporator condensate and the applicability of the system to full-scale plant operation.

The ability of high temperature MBR to treat kraft mill evaporator condensate has been proven by Bérubé (2000) who concluded: the optimal operating temperature and pH for a high temperature MBR are 60 °C and neutral respectively; 99 % methanol removal and 90 % TOC removal were observed during the treatment of kraft evaporator condensate by MBR. However, the MBR used in his study was operated under low mixed liquor volatile suspended solids (MLVSS) concentration (2500 mg /L while commonly achievable MLVSS concentration in a MBR is 10,000 to 30,000 mg/L) and low methanol loading (900 mg methanol/L condensate and 18-hr hydraulic retention time). Therefore, a steady state experiment was proposed to examine the performance of the high temperature MBR under the operating conditions proposed by Bérubé (2000) for a full-scale MBR system. Based on the results of Bérubé's study (2000), the operating parameters for the steady state experiment for the present study were selected as following: 38-day sludge retention time (SRT) and 9-hr hydraulic retention time (HRT) with kraft evaporator condensate that contained 1,200 mg methanol /L condensate.

An in-mill process water treatment plant would have to cope with non-steady state loadings resulting from the dynamic operating conditions at kraft mills. The volume and

strength of the wastewater, and unexpected incidents such as spills may have deleterious effects on the biological treatment process. In addition, the treatment system may need a long periods of start-up time after mill shutdowns for maintenance. Therefore, the ability of a treatment system to achieve satisfactory removal efficiency following shock loads and after mill shutdown is an important criterion for evaluating its suitability for full-scale implementation.

The effects of transient operating conditions on the high temperature MBR system performance are the other main interests of the present study. Considering the possible transient conditions that might cause upset of a treatment system in a kraft pulp mill, the present study proposed to investigate the effects of methanol organic shock loadings, black liquor carryover, and mill shutdown on the performance of high temperature MBR.

In summary, the objectives of the present research are listed below.

1. Investigate the performance of a bench-scale, high temperature MBR treating kraft mill evaporator condensate, with respect to removal efficiencies of methanol and total organic carbon (TOC), and biomass concentration in the MBR.
2. Identify the effects of methanol shock loadings on the performance of the high temperature MBR.

3. Determine the effects of black liquor carryover on the performance of the high temperature MBR.
4. Evaluate the capability of the high temperature MBR to cope with a mill shutdown and to recover in a reasonable time frame.

Chapter 4 Experimental Methods and Apparatus

4.1 Experimental Setup

4.1.1 Membrane Bioreactor

A schematic of the two MBRs used for the study is presented in Figure 4.1. Each membrane bioreactor consisted of an aerated reactor tank and a ceramic tubular ultrafiltration membrane. A progressive cavity pump (Moyno Model SP 33304) continuously circulated the mixed liquor through the membrane module and forced solid-liquid separation under trans-membrane pressure (30 psi, 200 kPa). Permeate from the membrane unit, controlled by level control devices, was wasted or recycled back to the reactor to maintain liquid volumes.

Two bench scale reactor tanks, both with 1.8 litre working volumes, were used and are shown in Picture 4.1. They were constructed of stainless steel and insulated to minimize temperature fluctuations. Ceramic ultrafiltration membrane units (Membralox 1T1-70 bench scale filtration unit: 7mm ID, 0.0055 m² surface area, 500 angstrom pore size) were selected because of their proven sustainability under extreme operating conditions such as high temperature (Bérubé, 2000).

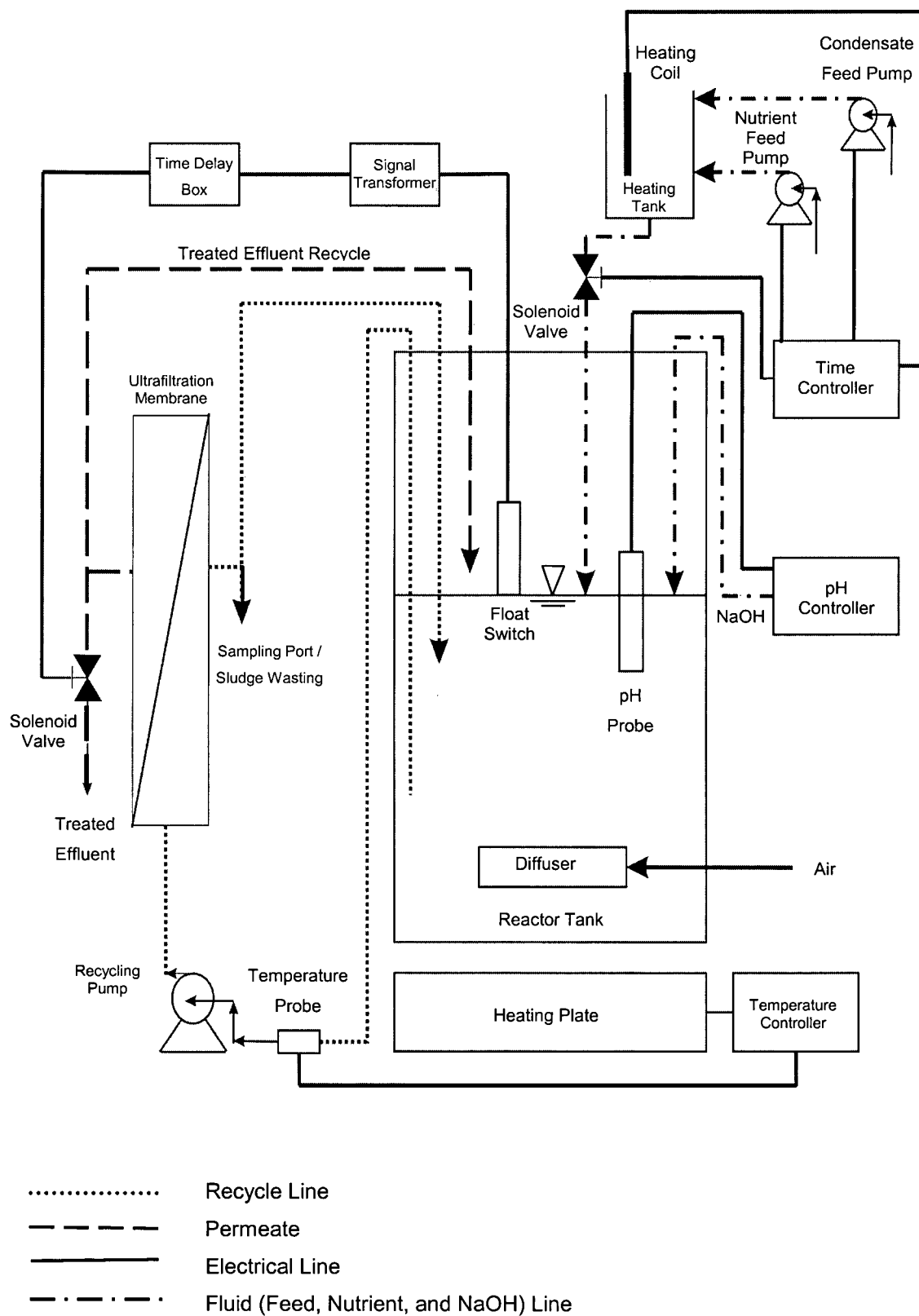
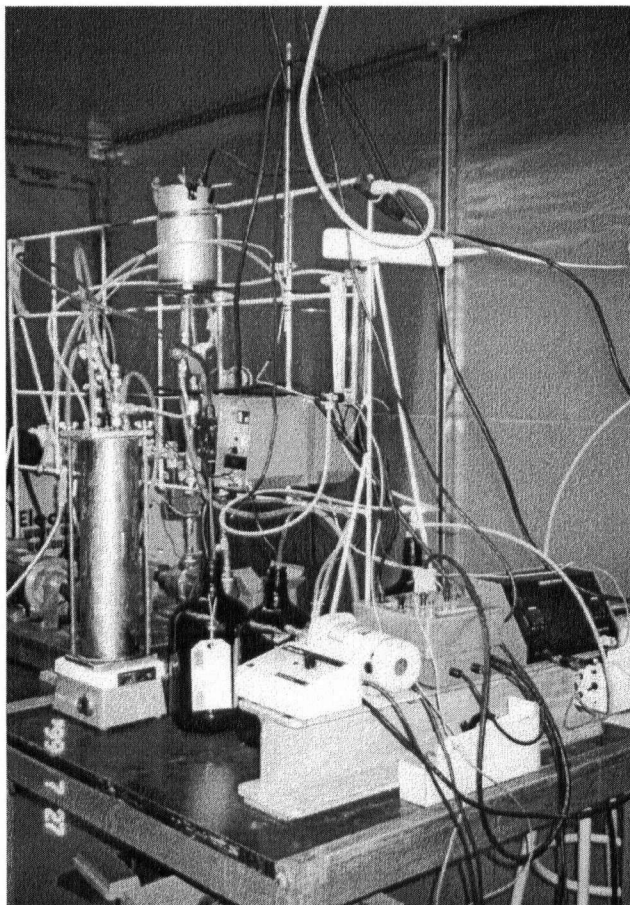


Figure 4.1 Schematic of Bench Scale High Temperature MBR



Picture 4.1 Bench Scale High Temperature MBR

4.1.2 Controlled operating conditions

4.1.2.1 pH

The pH of the mixed liquor in the MBR was controlled by a pH controller that added 2% sodium hydroxide solution automatically when pH was lower than the set point, 6.5.

4.1.2.2 Temperature

The temperature of the mixed liquor was maintained at 60 °C by a temperature controller and a heating plate. The reactor tank and the heating plate were placed inside a box constructed of insulation board to further minimize the temperature fluctuations. Moreover, before feeding, evaporator condensate was pre-heated until the temperature was equal to that of the operating temperature of the MBR. Therefore, the temperature fluctuation of the mixed liquor was controlled within ± 2 °C of the set point.

4.1.2.3 Mixing and Aeration

According to Bérubé (2000), to maintain non-limiting dissolved oxygen (DO) conditions, an aeration rate of 0.5 L/minute in the bench scale MBR was required as used for the present study. Non-limiting dissolved oxygen (DO) conditions were assumed when the zero order coefficients for the biological methanol removal were relatively constant.

Due to the instability of the available DO probe at elevated temperatures, the DO concentrations in the MBR could not be continuously monitored. Hence, the DO probe was used only during the setup period to ensure non-limiting DO conditions in the MBRs. A 0.5 L/minute of airflow was chosen and provided through a fine bubble diffuser in each reactor tank.

Mixing was provided by high the circulation rate between the reactor and the membrane component, and through aeration.

4.1.2.4 Permeate Flow

The permeate flow rate from both systems was monitored daily by collecting permeate in a graduated cylinder and calculating the volume filtered as a function of time.

4.1.2.5 Trans-membrane Pressure and Crossflow Velocity

The trans-membrane pressure on each system was maintained at 200 kPa (30 psi) and volumetric flow through the filter cartridge was controlled at 7 L/min to provide a crossflow velocity of 3 m/s at the membrane surface. The pump motor speed and the flow restriction valve on the downstream end of the recycling line of each MBR were adjusted daily to maintain these constant operating conditions.

4.1.2.6 Sludge Retention Time (SRT)

Commonly biomass concentrations in an MBR range from 10,000 to 30,000 mg/L (as mixed-liquor suspended solids, abbreviated as MLSS), and these high biomass concentrations allow high loading rates to MBRs. Therefore, relatively small reactor volumes will be required. During Bérubé's (2000) study, an observed growth yield of 0.2 and a biomass concentration of 2500 mg mixed-liquor volatile suspended solids

(MLVSS) per litre were measured when the sludge retention time was maintained at 20 days. Based on the result of Bérubé's (2000) research, a 38 day SRT was chosen for the present study, in order to achieve a MLVSS concentration of 10,000 mg/L. However, the effect of increasing the SRT on the observed growth yield wasn't considered in this calculation.

The solids retention time in each reactor was controlled by the wastage rate under steady state conditions. A 38-day SRT corresponded to 47 mL of daily wastage from the mixed liquor in each reactor.

4.1.2.7 Hydraulic Retention Time (HRT)

Because semi-continuous operation can provide more information about removal kinetics than experiments performed under strict continuous flow conditions, the MBRs were operated in a semi-continuous mode by feeding a mixture of evaporator condensate and nutrient, once every two hours.

The feeds of evaporator condensate and nutrient were pumped by Masterflex pumps to a 2-litre stainless steel tank. Then, the mixture was pre-heated for approximately 30 minutes with a stainless steel heating coil until the temperature was approximately equal to 60 °C. Subsequently, a solenoid valve, located at the bottom of the pre-heating tank, opened automatically to allow the mixture to flow into the MBR.

A hydraulic retention time of 9 hours was selected to achieve 95 % methanol removal efficiency, according to the specific methanol utilization coefficient estimated by Bérubé (2000). To maintain the selected HRT, a level control switch maintained a constant mixed liquor volume in each reactor tank. It directed the treated effluent (permeate) to a drain when the liquid volume in the reactor tank was above the setpoint, and recycled permeate back to the reactor tank when the setpoint liquid level had been reached. The level control switch was not activated until 30 to 60 minutes after the addition of the evaporator condensate in each feed cycle. During this period, permeate was recycled back to the reactor tank. The delayed wastage of permeate was designed to allow the bioreactor to have enough contact time with evaporator condensate to ensure maximal methanol removal. The start time of wasting at each cycle was controlled by a time delay box and was adjusted daily according to the permeate flow rate.

During experiments involving black liquor spill tests and the mill shutdown test, condensate was obtained from Howe Sound Pulp and Paper Limited (Port Mellon, BC, Canada). The Howe Sound condensate contained about 3-fold higher methanol concentrations than the condensate from the Western Pulp Limited Partnership bleached kraft mill (Squamish, Canada). To maintain an equivalent organic loading rate, the HRT was decreased four-fold.

4.1.2.8 Nutrients

Evaporator condensate contains some of the nitrogen required for the growth of microorganisms (Welander *et al.*, 1999), but lacks the metal ions necessary for healthy biological growth (Milet, 1998). Therefore, supplementation of nutrients may be necessary for achieving stable MBR operation when treating evaporator condensate.

The composition of the nutrient solution used in the present study (Table 4.1) remained constant throughout the study and was selected to ensure non-nutrient limiting conditions (Bérubé, 2000). To reduce the volume of nutrient solution added, the nutrient solution was concentrated 10-fold and 100 mL nutrient solution was added in the MBRs for every litre of condensate feed.

Table 4.1 Composition of Nutrient Solution

Nutrients	Nutrient Concentration per Litre of Condensate (Methanol Concentration = 1,200 mg/L) (mg/L)
NH_4NO_3	112.5
KH_2PO_4	76.5* (153)
$MgSO_4 \cdot 7H_2O$	25
$CaCl_2$	32.8
$FeCl_3 \cdot 6H_2O$	20

* According to Bérubé (2000), the amount of KH_2PO_4 was doubled to maintain required KH_2PO_4 concentration.

4.1.2.9 Source of Sludge and Evaporator Condensate

During the period of steady state testing and the methanol shock loading tests, the evaporator condensate was shipped from the Western Pulp Limited Partnership bleached

kraft mill (Squamish, BC, Canada) to UBC. Due to a shutdown of the Western Pulp mill, combined condensate was collected from Howe Sound Pulp and Paper Limited Partnership (Port Mellon, BC, Canada) during the black liquor spill tests and mill shutdown test. When received, kraft condensate was immediately sampled and characterized. Then, the condensate were acidified to a pH of approximately 4 with HCl, stored at temperature of 4 °C, and typically used within one week. The kraft condensate was transferred to a smaller 4 L sealed feed container, which was stored at 4 °C.

Throughout the study, the evaporator condensate received from Western Pulp Ltd., Squamish, was sampled and analyzed for methanol, TOC, pH, and conductivity. COD was characterized for the condensate from Howe Sound Pulp and Paper, Port Mellon. Condensate that had conductivity greater than 800 μ S was discarded. A high conductivity indicated the possible presence of black liquor entrainment in the evaporator condensate (personal communication, Pierre Bérubé, 2000) and that might affect MBR performance and consistency of experimental results.

4.2 Experimental Design

The intention of the study was to improve the understanding of process efficiency of the high temperature MBR and its applicability to full-scale plant operation. The experimental plan was divided into two phases. Phase I investigated the performance of the high temperature MBR treating condensate under the design conditions proposed by Bérubé (2000) for a full-scale plant. Phase II evaluated the effects of transient operating

conditions, which included methanol shock loadings, black liquor carryover, and mill shutdown, on the high temperature MBR system.

4.2.1 Steady-state Tests

According to research results reported by Bérubé (2000), a high temperature MBR treating evaporator condensate was designed to be operated under the conditions summarized in Table 4.2.

Table 4.2 Summary of Design Parameters (Bérubé, 2000)

Design Parameters	Value
Methanol Concentration (mg/L)	1,200
Operating temperature (°C)	60
pH	6.5
Sludge Retention Time (day)	38
Hydraulic Retention Time (hour)	9
Cross-flow velocity (m/s)	3
Trans-membrane pressure (atmosphere)	2
Time span of a batch cycle (hour)	2

By increasing the sludge retention time, a biomass concentration of 10,000 mg/L was expected to be reached in the MBR. Thus, the ability of the MBR to remove contaminants from evaporator condensate was anticipated to be maintained. MLVSS, the biological removal efficiency of methanol and TOC, growth yield, membrane permeate flow rate and colour removal efficiency were monitored throughout the test period.

4.2.2 Methanol Shock Loading Tests

The purpose of this test was to examine the response of the high temperature MBR to transients in organic loading rate, at constant HRT. Since real evaporator condensate was used as feed, the methanol concentration was adjusted by addition of exogenous methanol, to achieve different methanol loading rates.

In order to investigate the response to short-term and long-term shock loadings, Reactor 1 was subjected to four shock loadings to investigate long-term effects and Reactor 2 was subjected to one shock loading, to show short-term effects (Refer to Table 4.3). Condensate with concentrations of 150%, 200% and 250% of the steady-state methanol concentration (1200 mg/l) were used to generate the different shock loadings applied to the MBRs.

Table 4.3 Schedules of Methanol Shock Loading Tests

	Date	Influent Concentrations (mg/L)	Reactor 1 (Number of Feed Cycles with Shock Loading)	Reactor 2 (Number of Feed Cycles with Shock Loading)
Test 1	June 25, 2001	1800	4 (8 hrs)	1 (2 hrs)
Test 2	June 28, 2001	2400	4 (8 hrs)	1 (2 hrs)
Test 3	July 2, 2001	3000	4 (8 hrs)	1 (2 hrs)

4.2.3 Black Liquor Carryover Tests

The potential toxic effects of a black liquor entrainment to a high temperature MBR treating evaporator condensate were studied by these tests. The conductivity of

evaporator condensate increases dramatically with black liquor entrainment into the evaporator condensate and it can be used as an indicator. Volumes of 4 mL, 6 mL, 8 mL and 16 mL of black liquor in one litre of kraft condensate resulted in around 1000, 2000, 3000, and 6000 μS conductivity and these black liquor concentrations were chosen as the intensities of the black liquor shocks to be investigated.

During every black liquor carryover test, one reactor was subjected to four cycles of feed with black liquor addition to investigate long-term effects and the other was subjected to one cycle of feed with black liquor addition, to show short-term effects. However, among the four sets of black liquor carryover tests, each reactor received two long-term tests and two short-term tests to reduce the correlation between the test results to the extent possible (Refer to Table 4.4).

Table 4.4 Schedules of Black Liquor Carryover Tests

	Date	Influent Concentrations (mL black liquor addition/L)	Reactor 1 (Number of Feed Cycle with Shock Loading)	Reactor 2 (Number of Feed Cycle with Shock Loading)
Test 1	August 4, 2001	4	4 (8 hrs)	1 (2 hrs)
Test 2	August 7, 2001	6	1 (2 hrs)	4 (8 hrs)
Test 3	August 10, 2001	8	1 (2 hrs)	4 (8 hrs)
Test 4	August 16, 2001	16	4 (8 hrs)	1 (2 hrs)

4.2.4 Mill Shutdown Test

A kraft pulp mill is often shut down for 7 to 10 days for maintenance every year (personal communication, Jeanne Taylor, 2000, Western Pulp Limited Partnership, Squamish, B.C., Canada). To simulate the situation that a membrane bioreactor may face during mill shutdown, a 10-day-shutdown test was applied to reactor 2. Feeding and heating of the MBR system were terminated. Aeration and circulation rates through the membrane were reduced to one half of the normal values to maintain aerobic conditions in the reactor. During this 10 day period, a batch test was performed every two days to monitor the activity of reactor biomass. After the 10-day-shutdown test, the temperature was increased 10 °C every day until the original operating temperature of 60 °C was reached. Aeration and circulation rates through the membrane were returned to the original levels to maintain non-limiting dissolved oxygen (DO) conditions and mixing. During this re-start period, the MBR feed rate was increased from 25% of the original operating value to 100%, in 25% steps every day. Reactor activity was monitored during these four days.

4.3 Experimental and Analytical Methods

4.3.1 Biomass Acclimatization

During the start-up phase of the program, each MBR was inoculated with sludge from a full-scale activated sludge system treating kraft pulp mill effluent (Western Pulp Ltd.

Partnership, Squamish, B.C., Canada) and sludge from a pilot scale activated sludge system (UBC-Civil Engineering Pilot Plant, Vancouver, Canada). Approximately 500 mL of inoculum from each location were added directly to each MBR at approximately the same time and the reactor tank was topped-off with tap water. Since methanol is the most abundant compound in condensate, methanol was added to tap water to make up feed with a 1200 mg/L methanol concentration. When the systems were acclimatized to synthetic feed after two weeks, the MBRs were switched to 25% real evaporator condensate, 50% and finally 100% real evaporator condensate for a week respectively. The composition of feed was based on calculations to maintain constant methanol concentration. To reintroduce microorganisms that might not be able to grow under the previous conditions during the acclimatization, 250 mL of activated sludge from Western Pulp Ltd. was added into each MBR whenever the feed ratio of real evaporator condensate was changed.

4.3.2 Membrane Cleaning

The permeate flow rate through the membrane decreased with time. When the permeate flow rate was close to the rate that was just sufficient to accommodate the influent flow rate, membrane cleaning was performed based on the recommendation of the supplier and Bérubé (personal communication, 2000). The cleaning procedure required approximately 2 hours, and membrane runs lasted 1 to 9 weeks, depending on the nature of the membrane and the experiments.

4.3.3 Sampling and Sample Preparation

Mixed liquor samples were taken directly from the reactor and analyzed immediately. Feed samples were obtained from the pre-heat tanks just before introduction into the reactor. Permeate samples were collected from the membrane cartridge permeate port (See Figure 4.2 and Figure 4.3). The membrane casing was drained before sampling to minimize the dilution effect that can occur in the membrane casing. Since permeate samples were already filtered through the membrane unit ($0.05\ \mu\text{m}$), they did not require filtration before analysis and therefore, simplified analytical methods were applied.

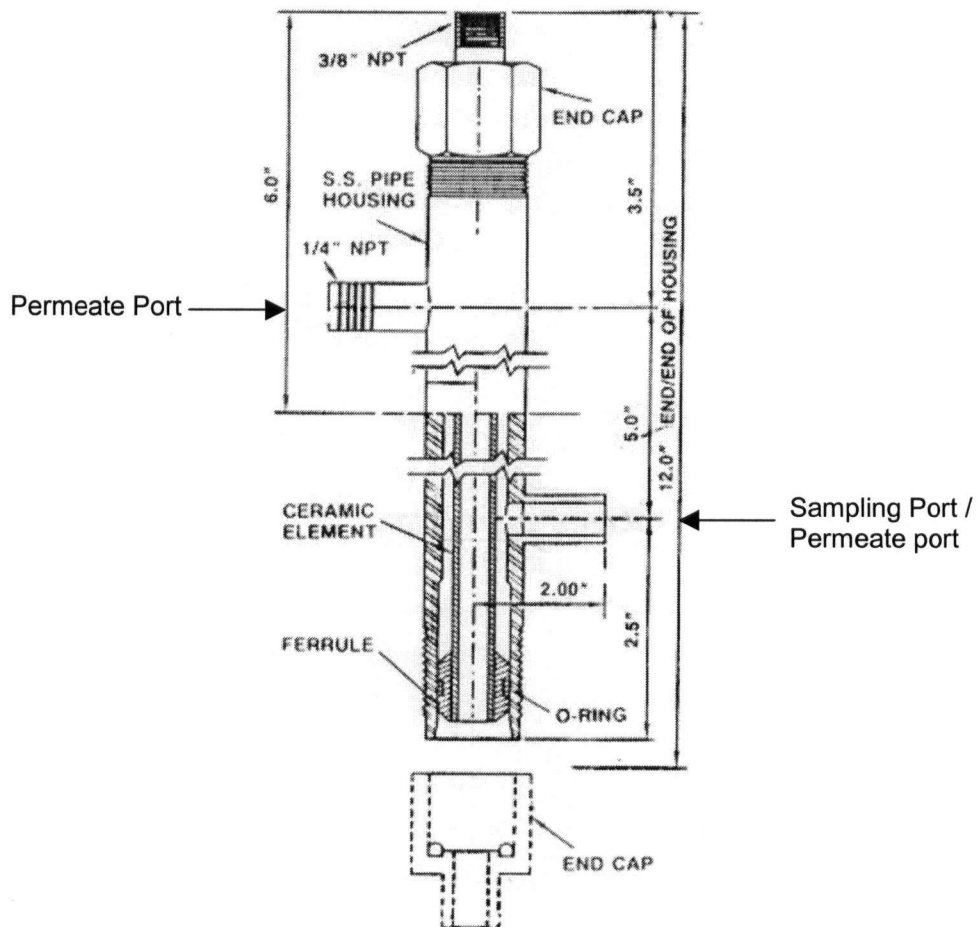


Figure 4.2 Membrane Unit Used for R1 and Partly for R2 (Membralox IT-70)

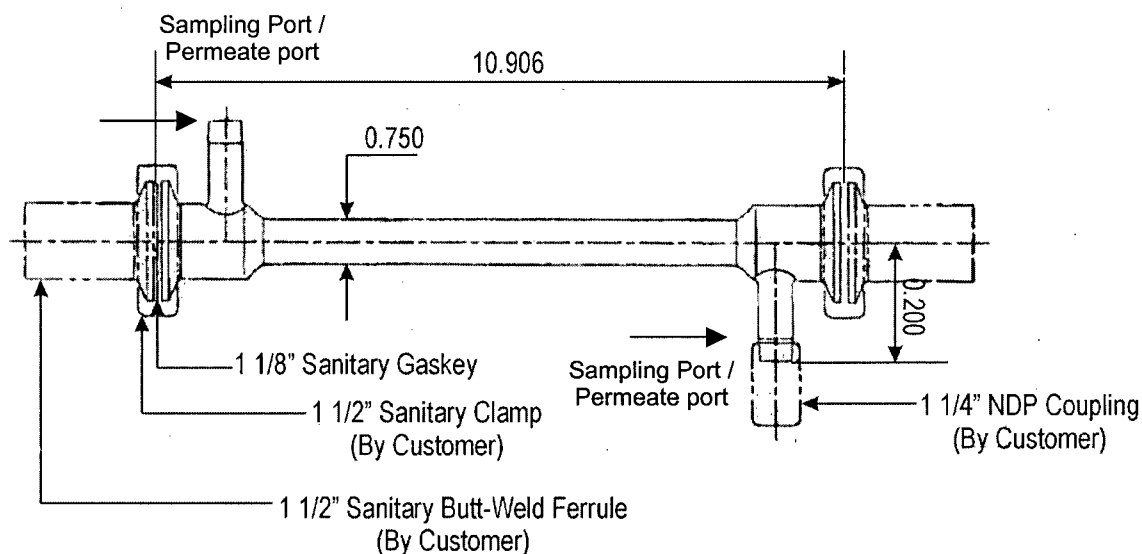


Figure 4.3 New Membrane Unit Used for R2 (Membralox IT-70)

4.3.4 Analytical Methods

4.3.4.1 Chemical Oxygen Demand (COD)

Condensate and feed samples were analyzed for total COD (TCOD) and dissolved COD (DCOD). Samples for DCOD analysis were filtered through $0.45\ \mu\text{m}$ cellulose nitrate membrane filters. Because the pore size of the membrane unit ($0.05\ \mu\text{m}$) was smaller than that of the cellulose nitrate membrane filters, TCOD was assumed to be equivalent to DCOD for effluent samples. Then, samples were diluted to fall into the range $0 \sim 900\ \text{mg/L}$ COD according to an estimation of sample strength. Samples were prepared and analyzed using a closed reflux colorimetric procedure with mercuric chloride addition as per Standard Methods 5220D (APHA/AWWA/WEF, 1995). After digestion in a Hach COD block digester, the absorbance of the samples and standards was measured at 600

nm using a Hach DR-2000 spectrophotometer. According to the standard curves and absorbance of the samples, COD in the samples were determined.

4.3.4.2 Conductivity

After the samples were acclimatized to ambient temperature (approximately 20 °C), the conductivity was measured using a Radiometer Copenhagen CDM3 conductivity meter.

4.3.4.3 Colour

True colour and apparent colour of permeate and feeds were evaluated using Standard Methods 2120B (APHA/AWWA/WEF, 1995). Colour readings were made using a Hach colour comparator. Because the colour and the pH of samples were highly related, both were recorded.

4.3.4.4 Methanol Concentration

Before analysis, feed and condensate samples were filtered through 0.45 μm cellulose nitrate membrane filters. The concentration of methanol was measured by direct injection of samples into a gas chromatograph (HP6890, Hewlett Packard Co.) with a 30 m long wide bore capillary column (Bérubé, 2000) and flame ionization detector, using 1-butanol as an internal standard.

4.3.4.5 pH

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

4.3.4.6 Total Organic Carbon concentration (TOC)

Condensate samples were analyzed for total organic carbon (TOC) and filtered TOC (FTOC). FTOC was assumed to be equivalent to TOC for permeate samples. Samples were filtered through a 0.45 μm cellulose nitrate syringe membrane filter cartridge before analysis of FTOC. The concentrations of TOC and FTOC were measured by combustion-infrared methods using the TOC analyzer (Shimadzu TOC-500) according to Standard Methods 5310B (APHA/AWWA/WEF, 1995).

4.3.4.7 Solids

Solids analyses followed Standard Methods 2540 (APHA/AWWA/WEF, 1995). Feed samples during black liquor tests were analyzed for total solids (TS), total volatile solids (TVS), total dissolved and colloidal solids (TDCS), and total volatile dissolved and colloidal solids (TVDCS). The permeate samples during black liquor tests were analyzed for TDCS. Samples from the mixed liquor of the membrane bioreactor were analyzed for total suspended solids (MLTSS) and volatile suspended solids (MLVSS).

Chapter 5 Results and Discussions

In this section, data and results obtained under steady and transient operating conditions are presented and discussed.

5.1 Characteristics of Condensate

During the period of steady state testing and methanol shock testing, evaporator condensate shipped from the Western Pulp Limited Partnership bleached kraft pulp mill in Squamish, British Columbia, Canada, was used. Due to a long period of Western Pulp mill shutdown, combined condensate was sampled from Howe Sound Pulp and Paper Limited (Port Mellon, BC, Canada) and used during the period of the black liquor carryover tests and the mill shutdown test. The characteristics of condensate used throughout the study were monitored and are summarized in Table 5.1 and Table 5.2 (Raw data are presented in Appendix 1).

Table 5.1 Characteristics of Evaporator Condensate from Western Pulp Ltd.

Measurement	Units	Average	90%* (+/-)	Number of samples
Conductivity	μS	381	44	39
pH		7.7	0.2	39
Methanol	mg/L	380	31	39
TOC	mg C/L	326	25	39
Filtered TOC	mg C/L	297	24	39
TOC solids**	%	9.3	2	39
Methanol as TOC	%	45.4	3	39
COD	mg O ₂ /L	1027	126	39

* 90% confidence interval

** TOC in the form of suspended solids

Table 5.2 Characteristics of Combined Condensate from Howe Sound Pulp Ltd.

Measurement	Units	Average	90%* (+/-)	Number of samples
Conductivity	μS	483	27.4	3
PH		8.4	0.19	3
Methanol	mg/L	4953	108.0	3
TOC	mg C/L	2085	95.0	3
Filtered TOC	mg C/L	1923	48.7	3
TOC solids	%	7.6	4.1	3
Methanol as TOC	%	89	6.0	3
COD	mg O ₂ /L	9303	114.1	3

* 90% confidence interval

** TOC in the form of suspended solids

Since the methanol concentration in the Western Pulp condensate was much lower than the design conditions (1200 mg/L), the Western Pulp evaporator condensate was spiked with methanol to a concentration of approximately 1200 mg/L before use.

5.2 MBR Operating Parameters

Temperature, trans-membrane pressure, crossflow velocity, pH, and SRT were independently controlled for this experiment, except for the mill shutdown test. These operating parameters can significantly influence the performance of the membrane bioreactors and were maintained as constant as possible.

5.3 Start-Up and Steady-State Operation

Two bench scale MBRs (called R1 for Reactor 1 and R2 for Reactor 2), described in Section 4.1.1, were used to investigate the performance of MBRs treating kraft evaporator condensate under steady state conditions. Based on Bérubé's (2000) research

results, the operating conditions for a high temperature membrane bioreactor were selected (referred to Table 4.2). HRT and SRT were maintained as 9 hours and 38 days respectively. After approximately 6 weeks of acclimatization, the methanol removal kinetics, total organic carbon removal kinetics, and suspended solids concentrations in the systems were monitored for 34 weeks.

The performance of the MBRs under steady state conditions was compared with the predictions from Bérubé (2000) and details are discussed below. A steady state condition was assumed to have been achieved when the concentration of mixed liquor volatile suspended solids (MLVSS) and the rate of the methanol removal in the MBR were relatively constant.

Various incidents occurred during the first 150 days while operating the membrane biological reactor and these are listed in Appendix 2. Mostly, they were due to spills caused from foaming problems and the breakdown of equipment. Excessive foaming was initially observed during the experimental period. To reduce foaming, a shower head on the return line and an insulation box around the reactor unit were installed for each MBR system. The foaming problem was well controlled after these changes.

Due to several serious upsets during the first 150 days of the experimental period, the performance of the two MBRs was significantly affected and the resulting data can't realistically represent the performance of an MBR under steady state conditions, as presented in Figure 5.1. Hence, only the data collected after day 150 for Reactor 1 (R1) and Reactor 2 (R2) were used in assessing MBR performance at steady state.

5.3.1 Methanol Removal

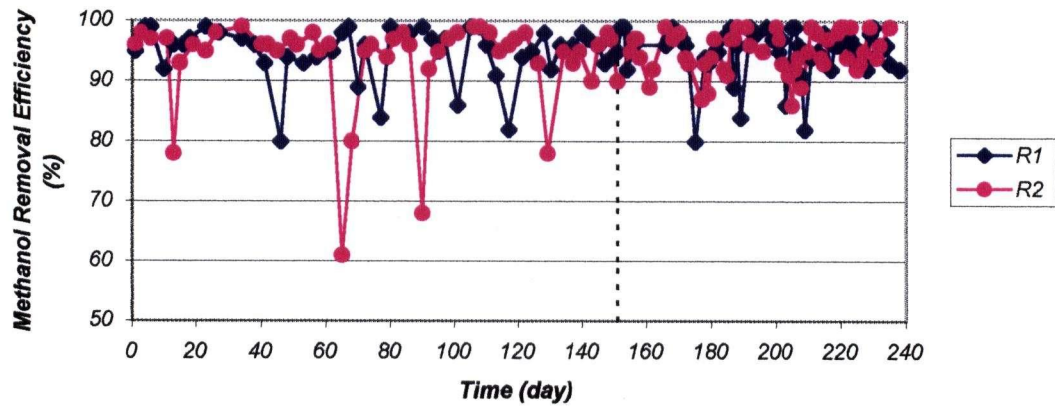


Figure 5.1 Methanol Removal Efficiencies of MBRs

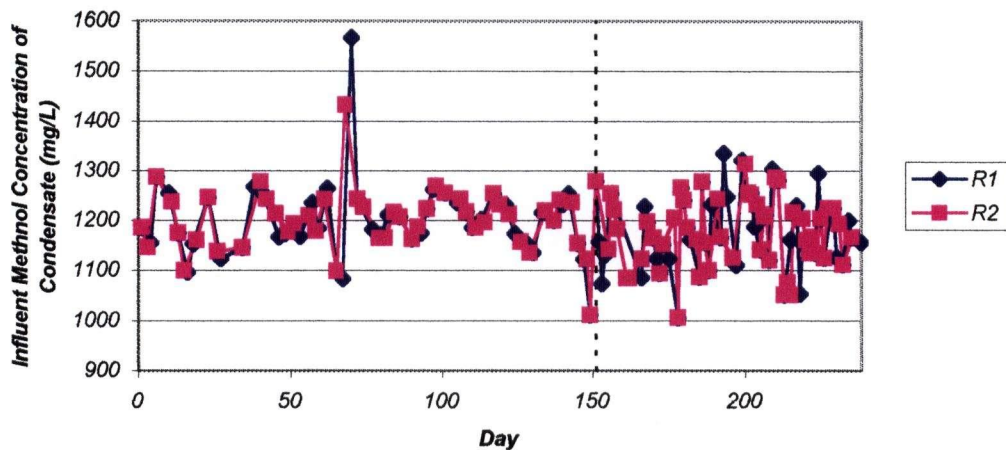


Figure 5.2 Methanol Concentration of Influent (Condensate Feed)

As shown in Figure 5.2, methanol concentration in the influent (condensate) was maintained relatively constant at a level of about 1,200 mg/L. However, various incidents, including high methanol concentration of influent, resulted in fluctuating

average effluent concentration and methanol removal efficiency before Day 151, as shown respectively in Figure 5.3 and Figure 5.1.

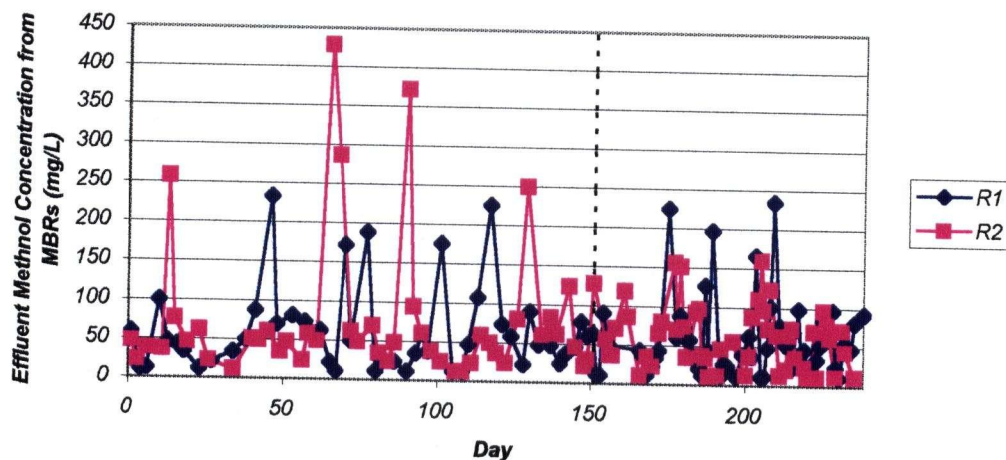


Figure 5.3 Average Methanol Concentration of Effluent

During a typical batch cycle, a volume of 400 mL condensate with a methanol concentration of 1,200 mg/L was added to the reactor containing a liquid volume of 1.8 L at the beginning of each feed cycle. This resulted in approximately 260 mg/L of methanol in the reactor. The concentration of methanol in the MBR was then reduced from approximately 260 mg/L to below the analytical method detection limit of 0.5 mg/L, as illustrated in Figure 5.4. Notably, before methanol in the reactor was fully biodegraded, part of the methanol was wasted with the permeate. Therefore, the average methanol concentration in the effluent was not zero, although all methanol in the reactor was removed by the end of the batch cycle. The average methanol concentration in the effluent was determined for the total volume of effluent collected from a feed cycle.

Methanol removal kinetics similar to those reported by Bérubé (2000) and Milet (1998) were observed throughout the steady state experimental period and the methanol removal rate achieved by the membrane bioreactor was estimated by using a zero-order relationship as presented in Equation 5.1.

$$R_{MeOH} = U_{MeOH} \cdot X = K_{MeOH} \quad (5.1)$$

where R_{MeOH} is the rate of biological removal of methanol (mg/L·min), U_{MeOH} is the specific methanol utilization coefficient (/min), K_{MeOH} is the zero-order coefficient for the biological removal of methanol (mg/L·min), and X is the concentration of MLVSS of MBR (mg/L)

The zero-order removal rate indicated that the uptake of methanol by the mixed microbial culture was not limited or inhibited by the concentrations of methanol in the range of concentrations examined (from approximately 260 mg/L (100 mg/L expressed as TOC) to below the detection limit of 0.5 mg/L). In addition, according to Bérubé (2000), stripping of methanol is a first order reaction and methanol removal due to stripping of the aeration system only accounted for less than 1% of the mass of methanol removed from the MBR.

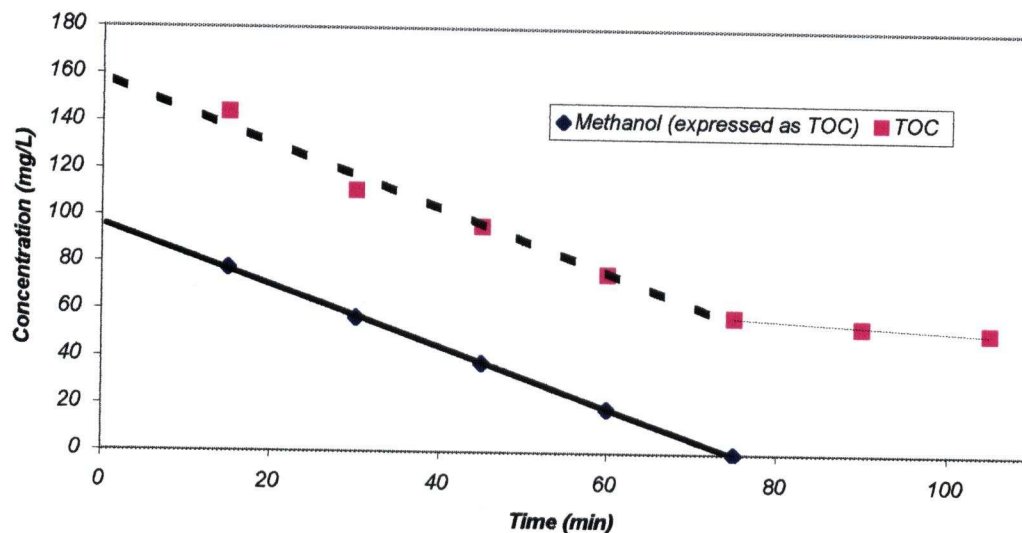


Figure 5.4 Concentrations of Methanol and Total Organic Carbon in MBR During a Typical Feed Batch Cycle (Methanol expressed as TOC)

During the steady state period of operation, the average methanol removal efficiency for R1 was 94.9 ± 0.94 % and for R2 was 94.8 ± 0.8 %, based on mass balance calculations for each the system (based on the data of Table A2-1 to A2-24 in Appendix 2). The average initial bioreactor methanol concentration in batch feed cycles for R1 and R2 was 257.3 ± 5.9 mg/L and the average effluent concentration was 12.9 ± 2.4 mg/L.

Due to the different calculation methods used in Bérubé's (2000) research and in the present study, the removal efficiency estimated from this study was slightly lower than Bérubé's (2000) results of 99%. However, the observed efficiency was still higher than the 90% removal achieved by the conventional technology, steam stripping. Removal efficiency calculated by Bérubé (2000) was the total biodegraded contaminant concentration in the reactor (the total mass of biodegraded TOC divided by total volume of the reactor) divided by influent contaminant concentration in the condensate (the total

mass of TOC of the feed divided by the total volume of the condensate added during a feed cycle). It should be noticed that the concentrations can't be used directly to calculate the removal efficiency since the volume of the reactor (1.8 L) and the volume of the condensate added during a feed cycle (400 ml) are different. Therefore, the contaminant removal efficiencies are higher from Bérubé's (2000) results.

Throughout the steady state period, the specific methanol utilization coefficients were estimated to be 1.03 ± 0.13 /day for R1 and 1.47 ± 0.15 /day for R2, which were 75 % and 150 % higher than Bérubé's result of, 0.59 ± 0.11 /day. The data are presented in Table A2-1 to A2-24 in Appendix 2. The higher specific methanol utilization coefficients of this study possibly indicated the higher methanol-utilization-capacity of the biomass because the biomass concentrations of both experiments were quite close to each other (Bérubé's (2000) biomass concentration was approximately 2,500 mg/L).

Following the start of each batch feed cycle, the pH in the MBR tended to decrease. This was also reported by Bérubé (2000) and he suggested that it was due to the production of CO₂ during the biological oxidation of methanol. This decline of pH was used as one of the indicators for the removal of methanol from MBR.

5.3.2 Total Organic Carbon (TOC) Removal

As illustrated in Figure 5.4, the concentrations of TOC in the MBRs were reduced from approximately 160 mg/L to approximately 50 mg/L during each batch feed cycle (172.1 ± 6.19 to 61.9 ± 3.83 mg/L for R1 and 161.92 ± 5.49 mg/L to 57.28 ± 3.16 mg/L). Similar

to Bérubé's observations, there was no significant further reduction in the concentration of TOC after methanol removal was completed (approximately 105 minutes after the start of the batch feed cycle). A relatively high residual concentration of TOC, 59.6 ± 5.9 mg/L, remained in the MBR, and the residual TOC was considered to be non-biodegradable organic matter.

Conclusively, 64 % of the organic material, measured as TOC, contained in the evaporator condensate could be removed by a high temperature membrane bioreactor. Comparing with the high TOC removal efficiency observed by Bérubé (2000) as 91 %, the TOC removal efficiency summarized during the present study was relatively low, but the difference between the results is mainly due to the different calculation methods used for removal efficiency (as mentioned in the last paragraph on page 48).

The TOC concentration in the MBR was modeled using two zero order sequential relationships as presented in Equation 5.1. Data from the tests and results from the linear regressions are presented in Appendix 2. The first specific TOC utilization coefficient (the slope of darker dashed line in Figure 5.4) was estimated to be 0.51 ± 0.072 /day for R1 and 0.74 ± 0.065 /day for R2. The results were close to 0.66 ± 0.056 /day, reported by Bérubé (2000).

5.3.3 Mixed Liquor Volatile Suspended Solids (MLVSS) Concentrations

To maintain a constant SRT, 47 mL of MBR mixed liquor was wasted daily. The resulting MLVSS concentration profiles of the two reactors throughout the steady state experiment are shown in Figure 5.5.

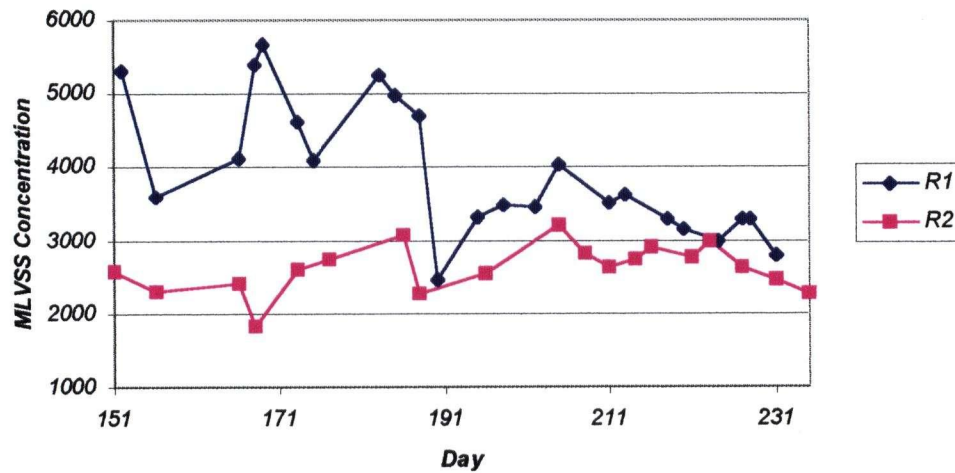


Figure 5.5 MLVSS Concentrations Throughout the Steady State Period
(After Day 151)

The observed growth yield was calculated following Equation 5.2 and details are included in Appendix 2.

$$Y_{obs} = \frac{\sum(Biomass)}{\sum(Methanol)} \quad (5.2)$$

where Y_{obs} : observed growth yield

$\sum(Biomass)$: Cumulative biomass production; total biomass wasted/sampled from the reactor and accumulated/decumulated in the reactor

$\sum(Methanol)$: Cumulative methanol removed; [(mass of influent methanol per batch) – (mass of permeate methanol per batch)] × (number of batches)

An observed growth yield of 0.2 mg MLVSS produced/mg methanol biologically removed was derived from Bérubé's (2000) research when treating bleached kraft mill evaporator condensate. An MLVSS concentration of 10,000 mg/L, was expected to be achievable in a high temperature membrane bioreactor with a 9 hr HRT and evaporator condensate with a 1200 mg/L methanol concentration. However, it is known that sludge production from biological aerobic wastewater treatment decreases with decreasing organic loading rates and increasing solids retention time (Henze et al., 1987). The steady state MLVSS concentration observed in the present study was approximately 3000 mg/L in R1 and 2500 mg/L in R2. The resulting calculated observed growth yields were 0.0347 for R1 and 0.0254 for R2.

Due to the nature of the bench-scale reactor set-up, wall growth of biomass in the reactor was observed, which affected the MLVSS concentration during the early stages of the experiment. To limit the wall growth and minimize the disturbance, scraping of the wall every two or three days was carried out throughout the study and it was found to effectively eliminate the wall growth.

Ragona (1998) reported that biomass from a membrane bioreactor was able to pass through the filter used for the determination of suspended solids according to Standard Methods (APHA/AWWA/WEF, 1995). As an alternative for suspended solids measurement, she subtracted the total solids concentration (which is equivalent to dissolved solids) in the permeate from the total solids concentration in the mixed liquor of the reactor to obtain the suspended solids concentration in the mixed liquor. Comparing the solids concentrations estimated in the two different ways, she found the MLVSS concentration estimated by the alternative method appeared to be a better indication of biomass. In the present study, dark or gray colour was observed from the liquid passing through the filter and it indicated that fine suspended solids possibly passed through the filter. However, this information was found almost at the end of the present study and since the solids determination followed Standard Methods, there are no appropriate data to confirm the findings of Ragona with the results of the present study.

Wouter and Willy (1999) reported that a substantially lower sludge yield (20 – 30 %) was observed in an MBR than in a conventional activated sludge system (CAS) under comparable conditions of influent concentration and volumetric loading rate. In addition, complete sludge retention achieved through membrane filtration may lead to grazing on bacteria by protozoa and metazoa in an MBR, since a higher abundance of flagellates and free ciliates was observed in an MBR than in a CAS (Wouter and Willy, 1999).

Uncoupled energy production and corresponding high maintenance energy for biomass are other possible explanations for the observed low growth yield in MBRs. Under certain conditions, more energy is produced than is required for anabolism and the excess

energy must be consumed by non-growth-associated processes. The phenomenon is called uncoupling (Horan, 1990), as the link between energy production and growth has been uncoupled. Low yield would be beneficial since it would reduce the cost of handling and disposal of biomass.

5.3.4 Summary

During the steady state period of the experiment, methanol and TOC removal efficiencies were 95 % and 64 % respectively. Compared with Bérubé's (2000) result (99 % methanol removal and 91 % TOC removal), the MBRs in the present study exhibited stable removal of the main contaminants. However, the difference between TOC removal efficiencies was due to the different calculation methods used for removal efficiency, as explained in 5.3.1.

With a long SRT (38 days), the MBRs exhibited a low observed growth yield, 0.0347 for R1 and 0.0254 for R2. Low growth yield is considered as an advantage of the process because of the low biosolids management cost.

Throughout the steady state period, the specific methanol utilization coefficients were estimated to be 1.03 ± 0.13 /day for R1 and 1.47 ± 0.15 /day for R2, which were 75 % and 150 % higher than Bérubé's (2000) result of, 0.59 ± 0.11 /day.

5.4 Methanol Shock Loading Tests

Methanol was identified as one of main contaminants of kraft condensate and methanol concentration fluctuates along with the evaporator operating conditions. To investigate the performance of a high temperature MBR under transient methanol loadings, MBR R1 was exposed to “long-term” methanol shock loading (8 hrs), and MBR R2 was exposed to “short-term” methanol shock loading (2 hrs), as described in Table 4.3 and Figure 5.6.

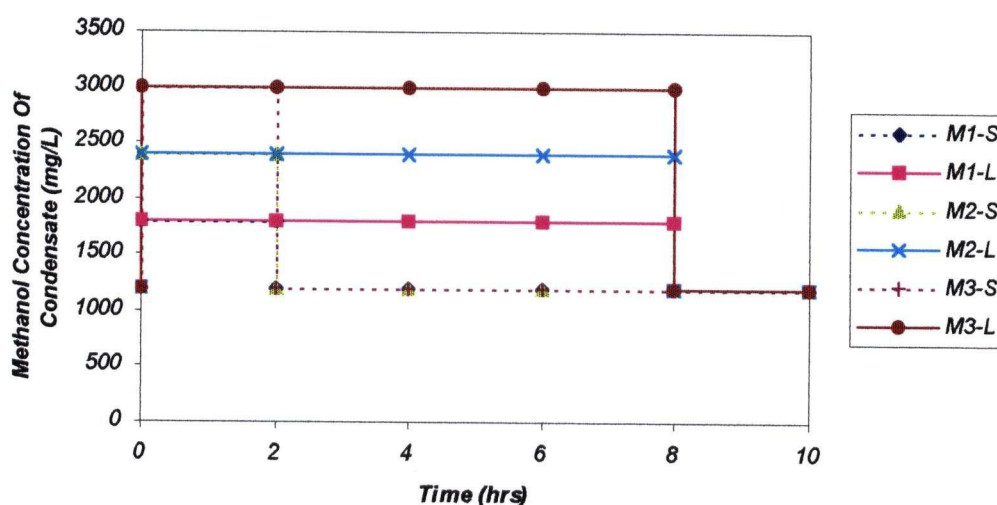


Figure 5.6 Initial Methanol Concentrations in Feed during the Methanol Shock Loading Tests (M: Methanol Shock Loading Test; L: Long-term; S: Short-term)

The effects of methanol shock loading on the high temperature membrane bioreactors were investigated by increasing the methanol concentration by factors of 1.5, 2, and 2.5. R1 was fed four consecutive batches (8 hours, close to 1 HRT that is 9 hrs) of feed with a higher concentration to study the long-term effect; R2 was fed one batch (2 hour) of high concentration feed to examine the short-term impact.

5.4.1 Methanol and TOC Removal

Results from the three methanol shock loading tests are summarized in Table 5.3 and details can be found in Appendix 3. Removal efficiencies of a feed cycle during periods of methanol shock-load testing are presented in Figure 5.7. Contaminant utilization coefficient profiles during the first, second, and third methanol shock loading test are shown respectively in Figure 5.8, 5.9, and 5.10

Table 5.3 Summary of Methanol Shock Loading Tests Results

Methanol Shock Loading Test		Initial Methanol Conc. In MBR (mg/L)		Final Methanol Conc. In MBR (mg/L)		Methanol Utilization Coefficient (mg/L·min)		Methanol Removal Efficiency (%)		Initial TOC Conc. In MBR (mg/L)		Final TOC Conc. In MBR (mg/L)		TOC Utilization Coefficient (mg/L·min)		TOC Removal Efficiency (%)	
Test	Batch	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
1	1	398	402	0	6	4.5	3.3	99	98	216	209	61	56	1.7	1.7	70	72
	2	405	259	0	0	3.8	2.9	99	99	172	138	64	33	1.1	1.0	61	75
	3	401	270	0	0	3.7	3.1	99	99	166	120	60	32	1.1	0.9	58	72
	4	388	281	0	0	3.5	3.2	99	99	154	128	60	31	1.1	1.0	60	66
	5	265	268	0	0	4.3	3.6	100	100	148	141	43	36	1.23	1.33	70	74
2	1	534	533	0	41	5.6	4.1	99	91	252	263	49	48	2.4	2.6	80	81
	2	536	268	0	0	6.0	4.6	99	100	208	95	56	34	1.7	0.9	72	63
	3	532	269	0	0	4.5	3.6	99	99	269	106	62	29	1.8	0.9	75	70
	4	510	238	90	0	3.5	3.5	81	99	240	106	108	32	1.1	1.0	52	69
	5	269	266	0	0	3.7	3.4	99	99	157	158	46	54	1.4	1.32	70	64
3	1	668	670	488	490	1.5	1.5	24	24	273	243	225	207	0.4	0.3	13	11
	2	1130	754	806	502	2.7	2.1	26	30	408	267	348	243	0.5	0.2	10	5
	3	1353	707	1029	479	2.7	1.9	21	29	540	259	516	199	0.2	0.5	1	19
	4	1672	685	1324	421	2.9	2.2	18	36	695	259	623	199	0.6	0.5	6	19
	5	1560	642	1188	385	3.1	2.5	21	38	637	191	505	131	1.1	0.5	17	28

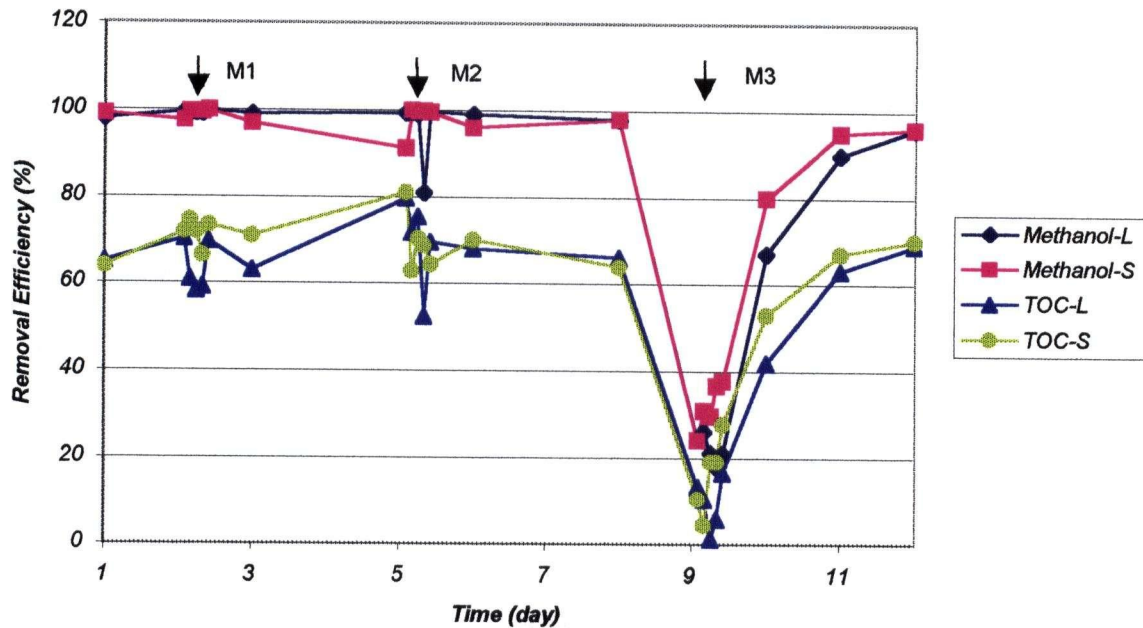


Figure 5.7 Contaminants Removal Efficiencies of the MBRs over the Methanol Shock Loading Tests Period (L: Long-term; S: Short-term; Time – 1st day: June 24, 2001)

As illustrated in Figure 5.8, there were no significant inhibitory effects on the performance of the MBRs, from either the long-term or short-term shock loadings. Methanol utilization coefficients of both MBRs increased as the methanol concentrations of the feed increased and returned to normal after the shock loadings were stopped. Removal efficiencies of both MBRs remained above 95% throughout the first methanol shock loading tests. Because methanol removal accounts for most of the TOC removal, TOC removal coefficients increased along with the methanol removal coefficients.

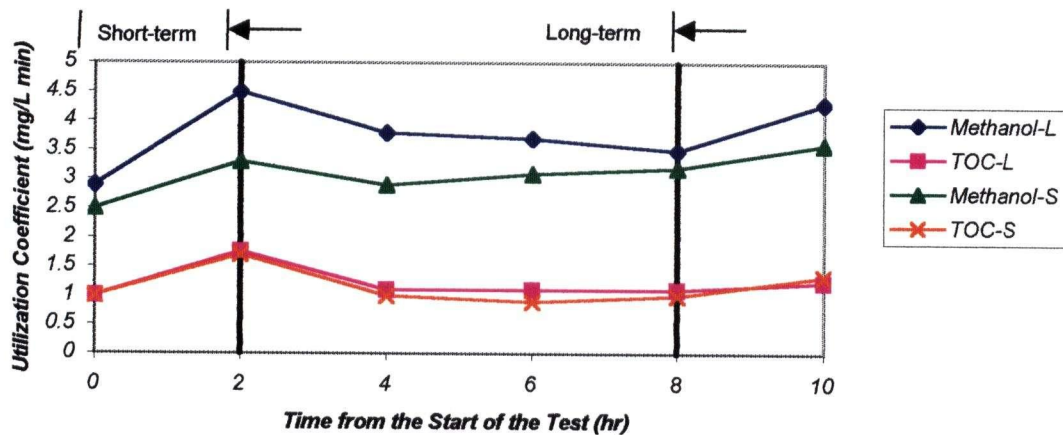


Figure 5.8 Methanol and TOC Utilization Coefficient Profiles during the First Methanol Shock-Loading Test
(Methanol Conc. = 1,800 mg/L; L: Long-term; S: Short-term)

Observed from Figure 5.9, for the second long-term methanol shock loading test, the methanol removal coefficient increased during the first feed cycle of the shock load, then decreased slightly. Since the methanol concentration of the shock load was much higher than that of the regular feed, the removal efficiency decreased even though the methanol removal coefficient remained above the initial value. Throughout the entire test, at least 95 % methanol removal efficiency was achieved in the MBR that received 4 batches of feed with a methanol concentration of 2400 mg/L. No negative effect on the MBR was observed from a short-term shock loading during the second methanol shock loading tests. These results showed that the MBR was reasonably stable to methanol organic shock loadings and maintained the same removal efficiency when the load was increased by 1.5 and 2 times instantaneously.

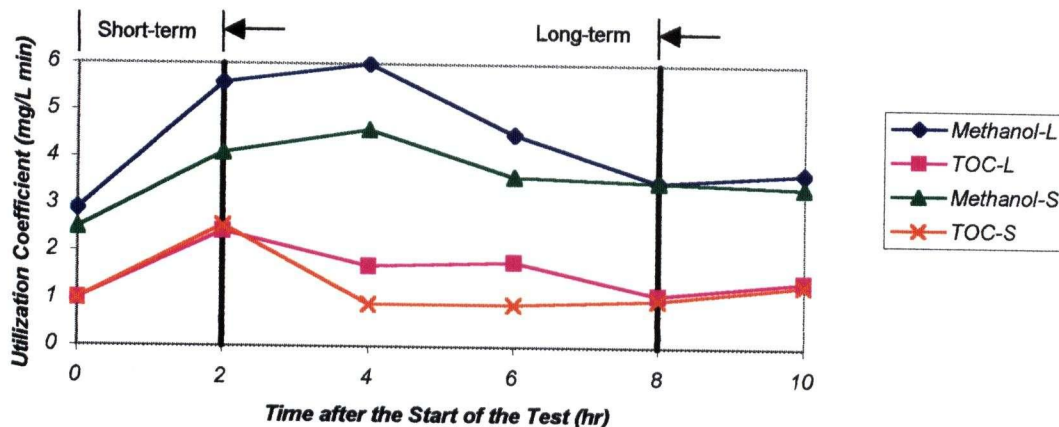


Figure 5.9 Methanol and TOC Utilization Coefficient Profile during the Second Methanol Shock-Loading Test

(Methanol Conc. = 2,400 mg/L; L: Long-term; S: Short-term)

When the feed strength was increased by a factor of 2.5, the methanol utilization coefficient of R1 (long-term test) dropped during the first feed cycle of shock load and increased slightly during the following shock loads, as shown in Figure 5.10. The methanol utilization coefficient of R2 (short-term test) decreased during the first feed cycle of shock load and gradually recovered once the shock loading was terminated. However, the MBRs showed distinct signs of overload, and couldn't biodegrade methanol fast enough so that the methanol concentration in MBRs increased after the shock loadings. There was unconsumed methanol present in the permeate and methanol and TOC removal efficiencies decreased to 21 % and 11 % respectively. About four hours after the short-term shock loadings, the methanol concentration in R2 returned to normal levels; the methanol concentration in R1 came back to the original concentration two days after the long-term shock loadings (refer to Figure 5. 7).

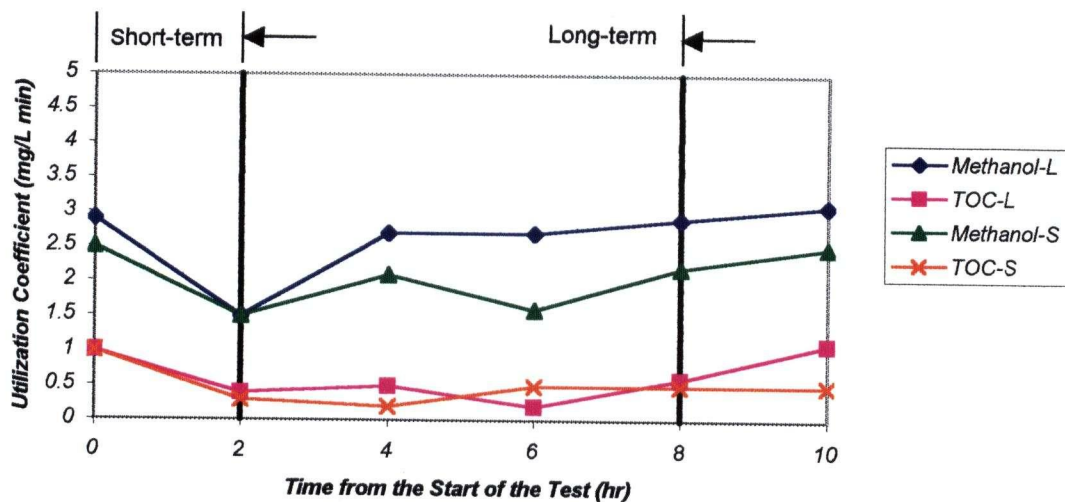


Figure 5.10 Methanol and TOC Utilization Coefficient Profile during the Third Methanol Shock-Loading Test

(Methanol Conc. = 3,000 mg/L; L: Long-term; S: Short-term)

A short-term shock loading didn't impose a serious effect on the high temperature MBR system and the system started to recover once the shock loading was terminated. The long-term shock loadings resulting from increased methanol concentration by factors of 2 and 2.5 times seemed to reduce the methanol removal efficiencies, but the system was still able to recover within 2 days.

Higher concentrations of methanol, as high as 4000 mg/L, have been reported by others to be non-inhibitory to a mixed culture (Koh *et al.*, 1989). On the other hand, dissolved oxygen (DO) was indicated as a rate-limiting factor for methanol oxidation (Shuler and Kargi, 1992; Milet, 1998). However, DO was not monitored throughout the present

methanol shock loading tests because of a temperature limitation for DO probe usage. Further research is needed to confirm the cause of the inhibitory effect from excess methanol concentration in the feed.

Conclusively, a high temperature MBR was stable to a perturbation of excess methanol concentration, and was able to absorb the overload and maintain the performance of the reactor until the loading rate was so high that it overloaded the system.

5.4.2 Colour Removal

As illustrated in Figure 5.11, the colour of the condensate was much higher than that of permeate, indicating that the ultrafiltration membrane was effective at rejecting some colour bodies. Since the nominal size of the ultrafiltration membrane (0.05 μm) was smaller than that of the membrane filter required for the filtration of the sample for colour determination, the apparent colour of the permeate was equivalent to the true colour of the permeate.

Addition of methanol didn't increase the colour of condensate. However, there was a slight increase of permeate colour after the third methanol shock loading test. Overload of methanol seemed to disturb the biomass and the upset reaction of biomass to degrade and oxidize the condensate organic matter probably produced this additional colour.

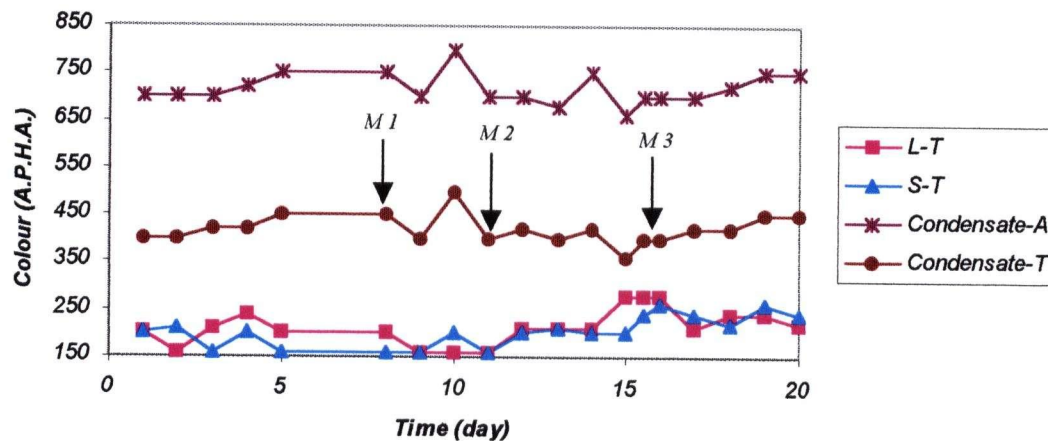


Figure 5.11 Colour of the MBRs Permeate and Condensate (Influent) over the Methanol Shock Loading Tests Period (M: Methanol Shock-Loading Test; A: Apparent Colour; T: True Colour; L: Permeate of MBR 1 (Long-term Shock Loading); S: Permeate of MBR 2 (Short-term Shock Loading); Time – 1st day: June 17, 2001)

5.4.3 MLVSS Concentrations

MLVSS concentration profiles of R1 and R2 are shown in Figure 5.12. Excess methanol from the methanol shock-loading tests seemed to increase the observed growth yields and the MLVSS concentrations in the MBRs. Except after the third methanol shock-loading test, biomass in R1 notably decreased and built up slowly in the reactor because of the overload of the system. The observed yield coefficients (0.0415 for R1 and 0.0334 for R2) were higher for both the long-term and short-term transient experiments.

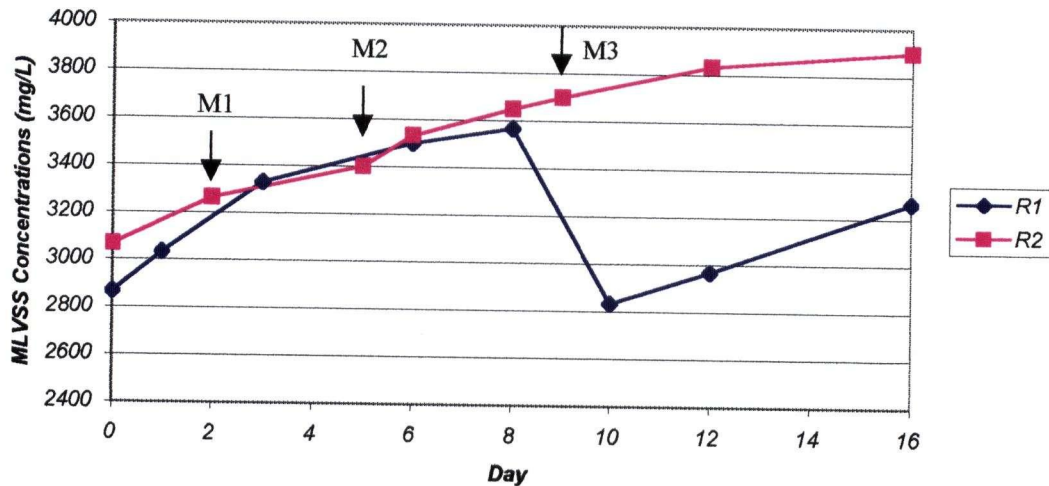


Figure 5.12 MLVSS Concentrations during the Methanol Shock Loading Tests
(Time – 1st day: June 23, 2001)

5.4.4 Summary

The MBRs were reasonably stable and able to maintain the same removal efficiency when the feed methanol concentration was increased by 1.5 and 2 times instantaneously.

When the feed strength was increased by a factor of 2.5, the MBRs showed distinct signs of overload. However, R1 recovered about four hours after the short-term shock loadings, and R2 functioned normally two days after the long-term shock loadings.

Overload of methanol seemed to disturb the biomass and the colour of the permeate slightly increased after the methanol shock loading test with 3,000 mg/L methanol concentration.

Excess methanol from the methanol shock-loading tests increased the observed growth yields and the MLVSS concentrations in the MBRs.

5.5 Black Liquor Carryover Tests

Although Best Management Practices (BMP) programs have been implemented by many mills to reduce the extent and frequency of liquor spills, it's difficult to fully eliminate spills from mill operations. Condensate used throughout the present study sometimes was found to have much higher conductivity than normal, and the high conductivity indicated the presence of a significant amount of black liquor entrainment into the condensate. (Personal communication with Taylor J., 2001, Western Pulp Limited Partnership, Squamish, Canada; Bérubé, 2000). A significant liquor spill typically increases the COD to an external secondary treatment plant by a factor of 3 to 4 (Personal communication, Doug Barton, NCASI, 2001), and it's important to determine whether a high temperature membrane bioreactor can survive spills or black liquor carryover of a similar magnitude. To simulate black liquor carryover, weak black liquor was collected from Howe Sound Pulp and Paper Ltd. (Port Mellon, Canada) and added into condensate at different ratios. The raw data, on which this discussion is based, are presented in Appendix 4. As shown in Table 4.4 and Figure 5.13, R1 and R2 were exposed to long-term and short-term black liquor carryover tests alternately during the black liquor carryover tests. The black liquor shock tests were separated in time by 3 to 6 days of normal operation (See Table 4.4). For the convenience of discussion, the results are presented by long-term and short-term tests.

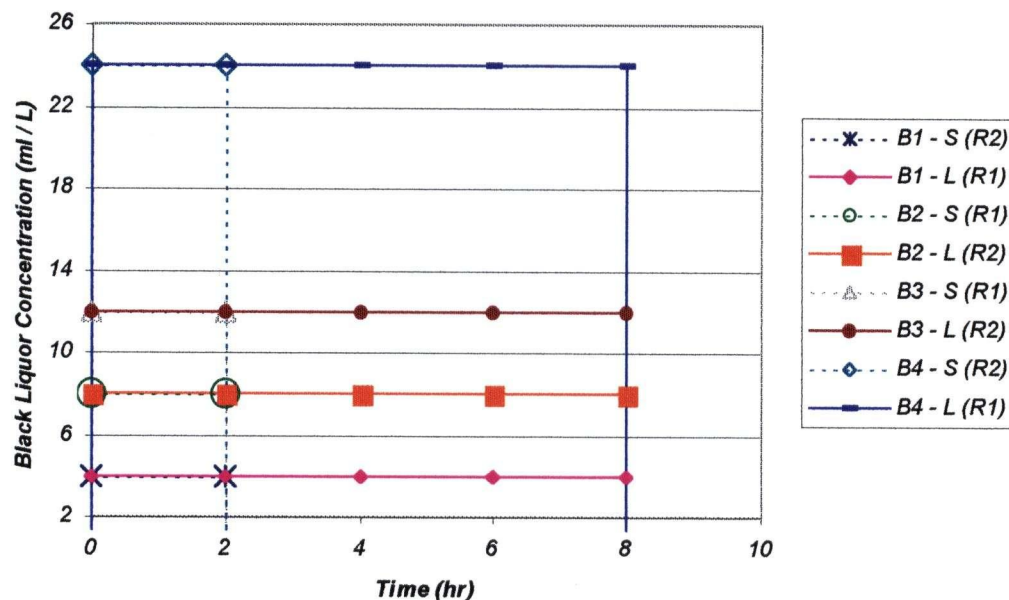


Figure 5.13 Black Liquor Concentrations during the Black Liquor Carryover Tests
(B: Black Liquor Carryover Test; L: Long-term; S: Short-term)

5.5.1 Characteristics of Condensate with Black Liquor Carryover

Black liquor is a complex mixture of water, inorganic salts, and organic matter. The characteristics of black liquor vary considerably with the operating conditions of mills and change significantly throughout different stages of evaporation and burning within a mill (Frederick *et al.*, 1980). Since the focus of the present study was on the effects of black liquor carryover on condensate treatment, not black liquor itself, the characteristics of black liquor weren't studied. Weak kraft black liquor was collected from Howe Sound Pulp and Paper Ltd. (Port Mellon, Canada) and added into condensate in different amounts. The characteristics of condensate with different amounts of black liquor addition are presented in Table 5.4. It is interesting to note that the TOC increased significantly with the volume of black liquor contained in the condensate while COD did

not increased accordingly. However, it is highly possible that it is due to experimental error when conducting the COD experiment.

Table 5.4 Characteristics of Condensate used for Black Liquor Carryover Tests

Sample	Conductivity (μ S)	TOC (mg C/L)	COD (mg C/L)	Filtered COD (mg C/L)	Filtered COD/COD (%)	TS (mg/)	TVS (mg/L)	TVS /TS (%)
Condensate	480	2085	9303	9205	99.5	1200	780	65
4 *	1000	2785	9671	9254	95.2	1880	1380	73.4
8*	2000	3420	9793	9354	95.5	2380	1620	68.1
12*	3000	4072	9965	9597	96.3	3080	2400	61.9
24*	6000	5896	10014	9840	98.3	4880	2860	58.5

* The number indicates the volume of mL black liquor per L condensate

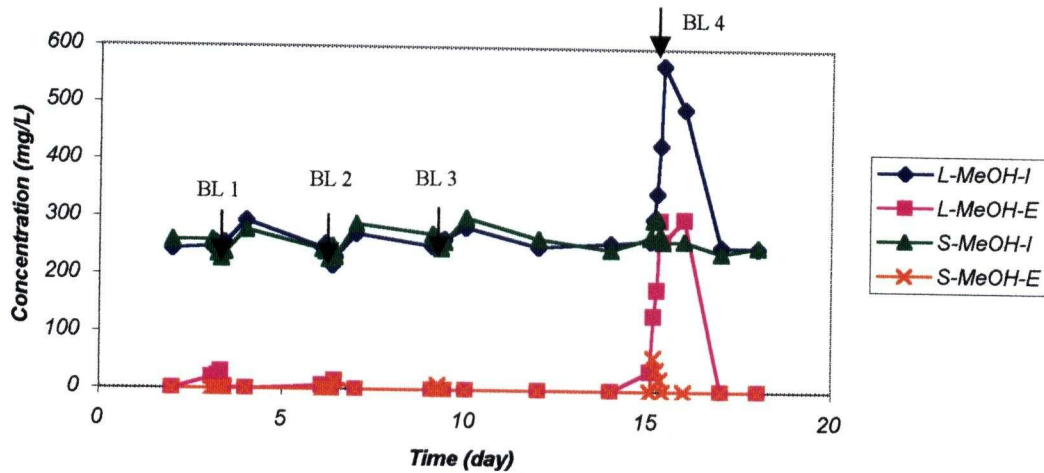
5.5.2 Methanol, COD, and TOC Removal

Results from the four black liquor carryover tests are summarized in Table 5.5. From Table 5.5 and Appendix 4, initial contaminant concentrations and final effluent contaminant concentrations in the MBRs of one batch cycle during the periods of black liquor carryover testing are presented in Figure 5.14. Contaminant utilization coefficient profiles during the first, second, third, and fourth black liquor carryover tests are shown respectively in Figure 5.15, 5.16, 5.17, and 5.18.

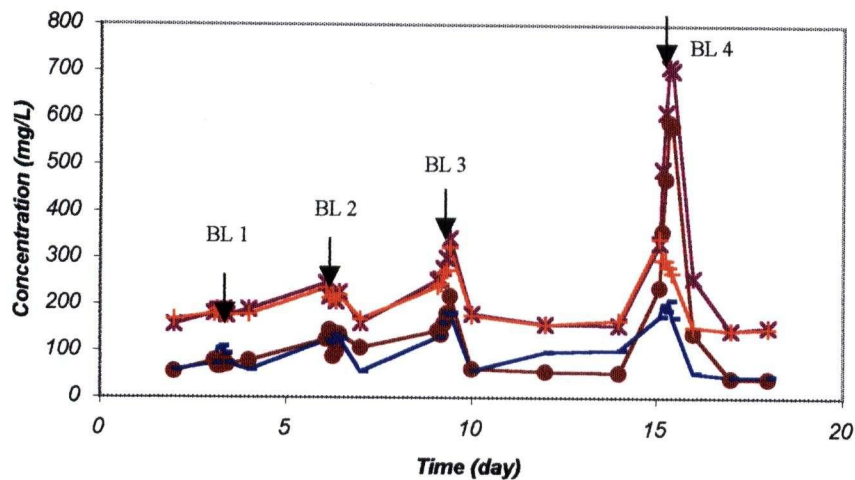
As shown in Figure 5.15 and Figure 5.16, the first and second black liquor carryover tests didn't have any significant effects on the MBRs, as a result of either the short-term or long-term shocks. The MBRs were able to degrade the excess COD and TOC and the methanol removal efficiency remained above 95 %.

Table 5.5 Summary of Black Liquor Carryover Tests Results

Black Liquor Carryover Test	Batch	Initial Methanol Conc. In MBR (mg/L)		Final Methanol Conc. In MBR (mg/L)		Methanol Utilization Coefficient (mg/L·min)		Initial TOC Conc. In MBR (mg/L)		Final TOC Conc. In MBR (mg/L)		TOC Utilization Coefficient (mg/L·min)		Initial COD Conc. In MBR (mg/L)		Final COD Conc. In MBR (mg/L)		COD Utilization Coefficient (mg/L·min)	
		R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
1	1	248	260	20	0	1.9	2.2	182	180	79	73	1.2	1.3	715	735	415	231	2.5	4.2
	2	255	253	15	0	2	2.3	188	189	68	105	1	0.7	735	711	507	207	1.9	4.2
	3	251	236	23	0	1.9	2	187	181	67	109	1	0.6	781	654	517	294	2.2	3
	4	246	227	30	0	1.8	2.6	190	178	82	94	0.9	0.7	828	616	384	220	3.7	3.3
	5	255	239	3	0	2.1	2.2	177	177	71	75	1.3	1.1	878	609	614	393	2.2	1.8
2	1	244	247	0	7	2.1	2	236	247	123	126	1.3	1.5	790	800	262	512	4.4	2.4
	2	241	254	0	0	2.3	2.2	214	218	118	146	0.8	0.6	802	1045	394	721	3.4	2.7
	3	227	240	0	0	2.5	2.1	219	221	135	89	0.7	1.1	812	1066	380	646	3.6	3.5
	4	250	217	0	0	2.4	1.9	209	207	125	99	0.7	0.9	790	982	394	562	3.3	3.5
	5	242	231	14	15	1.9	1.8	221	227	127	136	1.0	1.1	765	883	405	379	3	4.2
3	1	272	251	0	0	3	2.6	240	254	130	144	1.2	1.3	723	768	315	264	3.4	4.2
	2	268	250	0	0	2.4	2.9	246	256	162	136	0.7	1.0	714	840	342	324	3.1	4.3
	3	261	249	9	0	2.1	2.7	268	280	184	160	0.7	1.0	836	842	500	422	2.8	3.5
	4	247	261	0	0	2.4	2.4	275	302	179	182	0.8	1.0	884	849	404	333	4	4.3
	5	259	263	0	0	2.2	3.1	324	343	183	219	1.6	1.5	956	1008	464	420	4.1	4.9
4	1	263	269	35	0	1.9	2.3	334	344	238	176	0.8	1.4	920	956	488	488	3.6	3.9
	2	301	300	133	60	1.4	2	491	298	359	202	1.1	0.8	1040	936	656	480	3.2	3.8
	3	347	303	179	39	1.4	2.2	614	297	470	189	1.2	0.9	1169	922	821	454	2.9	3.9
	4	432	274	300	22	1.1	2.1	712	283	592	211	1.0	0.6	1314	884	1014	428	2.5	3.8
	5	571	262	391	0	1.5	2.4	703	270	583	174	1.0	0.8	1577	823	1289	307	2.4	4.3



(a) Methanol Concentration Profile



(b) TOC Concentration Profile

Figure 5.14 (a) and (b) Methanol and TOC Concentration Profiles during the Black Liquor Carryover Tests (L: Long-term; S: Short-term; MeOH: Methanol; I: Initial Contaminant Concentration in the MBR during a Batch Cycle; E: Final Effluent Contaminant Concentration in the MBR during a Batch Cycle; Time – 1st day: August 3, 2001)

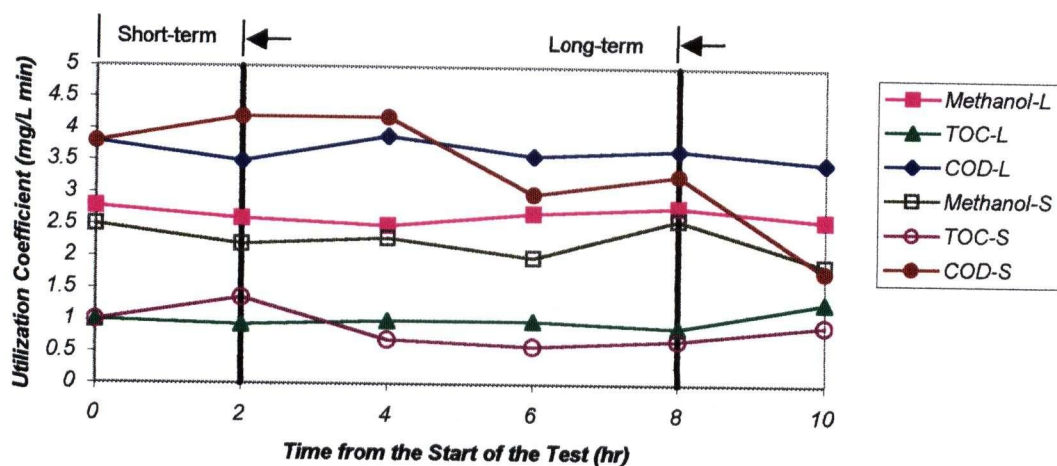


Figure 5.15 Methanol, TOC, and COD Utilization Coefficients Profiles during the First Black Liquor Carryover Test

(Black Liquor Concentration: 4 ml BL/ L condensate; L: Long-term; S: Short-term)

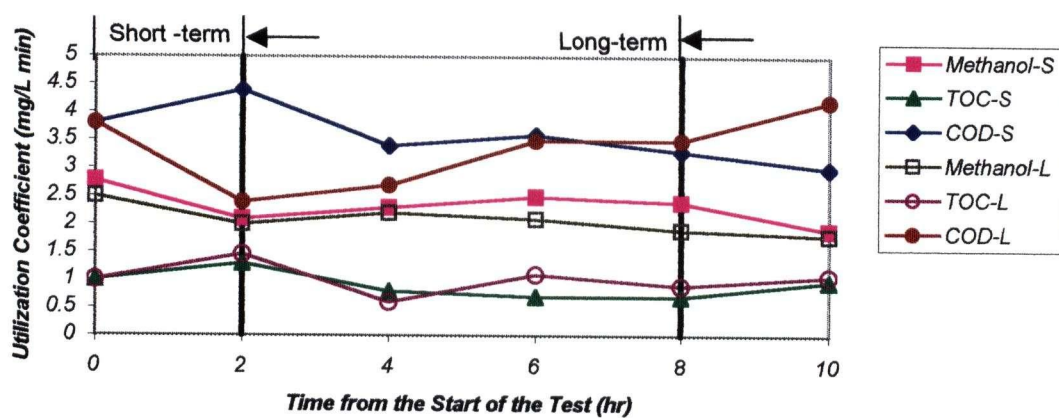


Figure 5.16 Methanol, TOC, and COD Utilization Coefficients Profiles during the Second Black Liquor Carryover Test

(Black Liquor Concentration: 8 ml BL/ L condensate; S: Short-term; L: Long-term)

As shown in Figure 5.17 and Table 5.5, an inhibitory effect was observed from the MBR exposed to the third long-term black liquor carryover test. The methanol removal coefficient continuously and gradually decreased throughout the third long-term black liquor carryover test. However, methanol removal efficiency still remained above 95 %. TOC, and COD removal efficiency decreased slightly and were 35 and 53 %, for the long-term black liquor carryover test.

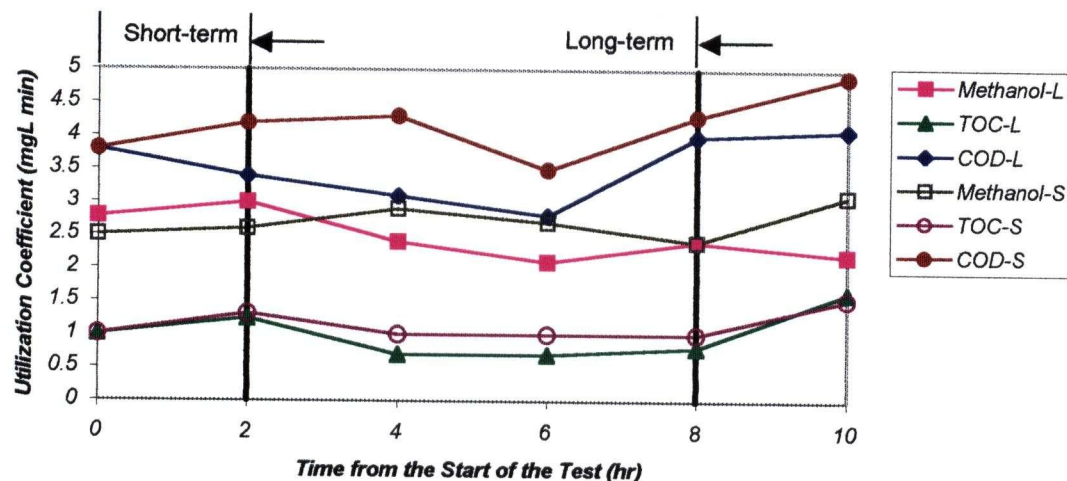


Figure 5.17 Methanol, TOC, and COD Utilization Coefficients Profiles during the Third Black Liquor Carryover Test

(Black Liquor Concentration: 12 ml BL/ L condensate; S: Short-term; L: Long-term)

As illustrated in Figure 5.18 and Table 5.5, there were deleterious effects on both MBRs from the fourth black liquor carryover test, both long-term and short-term. The methanol utilization coefficient of R1 that was subjected to a long-term test decreased by 50 % and

there was residual methanol observed in both MBRs. Since methanol removal accounted for most of the TOC and COD removal, TOC, and COD removal efficiencies dropped dramatically with methanol removal efficiency. As observed from Figure 5.14 and data from Appendix 4, for the short-term test, the MBR recovered relatively fast and the methanol concentration returned to normal levels after two feed cycles (4 hours). Comparatively, the long-term test upset the MBR and the system recovered only after two days of normal operation. Excess TOC and COD concentrations were observed in the MBRs.

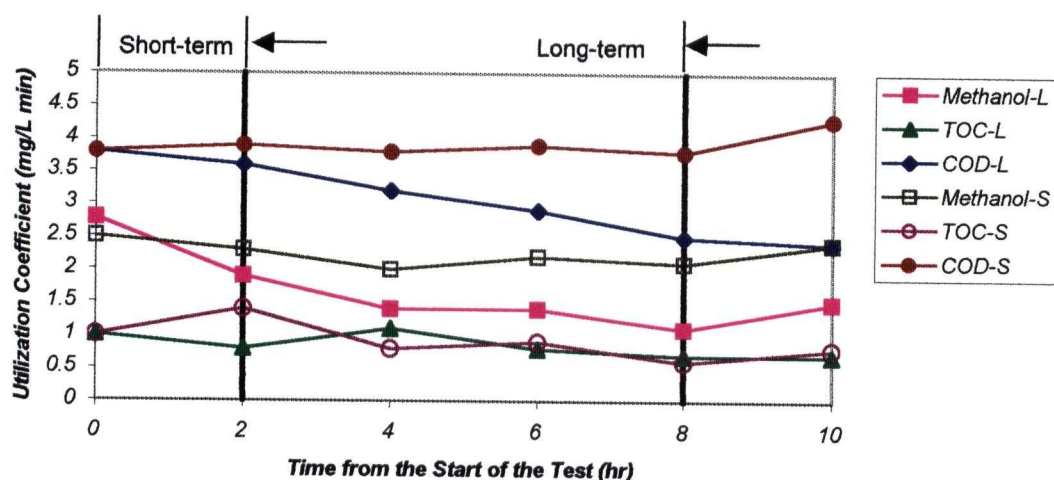


Figure 5.18 Methanol, TOC, and COD Utilization Coefficients Profiles during the Fourth Black Liquor Carryover Test

(Black Liquor Concentration: 24 ml BL/ L condensate; L: Long-term; S: Short-term)

5.5.3 Colour Removal

The colour of condensate used during this study was usually light brown and approximately 700 A.P.H.A of apparent colour and 400 A.P.H.A of true colour. With black liquor carryover, the colour of condensate turned darker and increased dramatically even with a small amount of black liquor addition. The addition of 4 mL black liquor in one litre of condensate increased the colour from 700 to 1000 A.P.H.A as apparent colour and from 400 to 700 A.P.H.A as true colour.

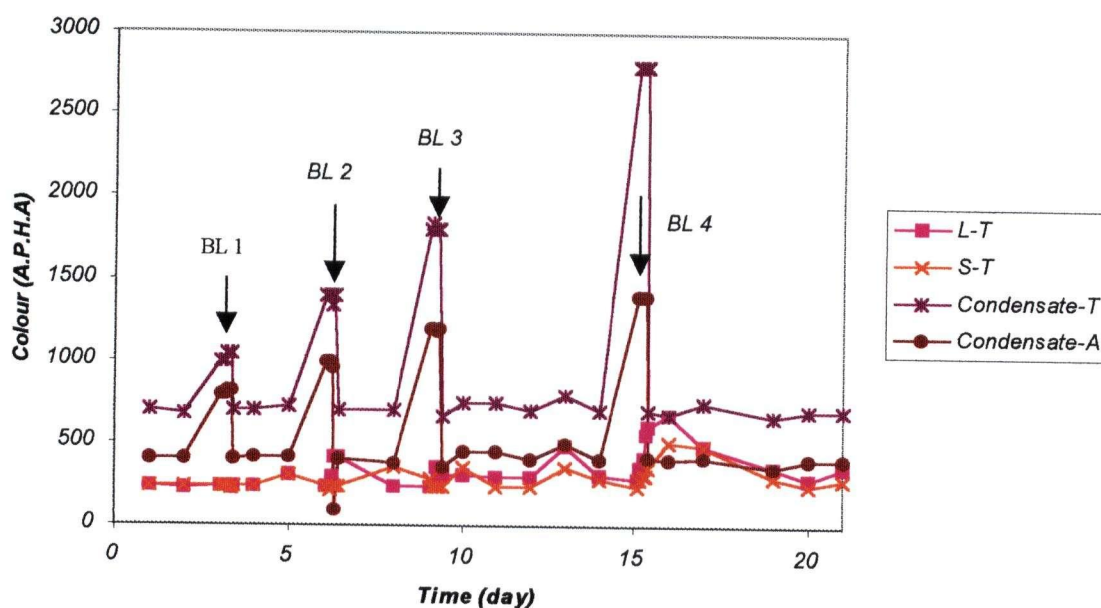


Figure 5.19 Colour of the MBRs Permeate and Condensate (Influent) over the Period of Methanol Shock Loading Tests (BL: Black Liquor Carryover Test; A: Apparent Colour; T: True Colour; L: Permeate of MBR Exposed to Long-term Shock Loading; S: Permeate of MBR Exposed to Short-term Shock Loading; Time – 1st day: Aug. 2, 2001)

The colour of the permeate remained relatively constant throughout the period of the black liquor carryover tests, as illustrated in Figure 5.19. The apparent colour and the true

colour of condensate with black liquor carryover increased from 700 to 2800 A.P.H.A and from 400 to 1300 A.P.H.A, but the true colour of permeate only increased from 250 to 400 A.P.H.A. The permeate colour returned to normal shortly after the tests were completed. However, black liquor carryover didn't significantly increase the colour of permeate. The MBRs showed great ability to cope with significant colour increase by black liquor carryover.

5.5.4 Solids Removal and Permeate Flux

The MBRs removed 100 % of suspended solids and suspended solids removal efficiency was not affected by black liquor carryover because the pore size of the membrane (500 Angstroms) was smaller than the filter size (1450 Angstroms) used in determination of suspended solids by Standard Methods (APHA/AWWA/WEF, 1995).

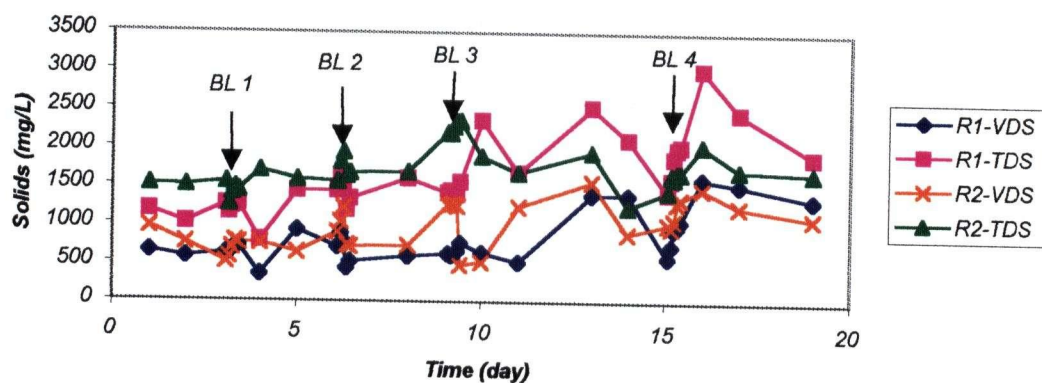


Figure 5.20 Volatile and Total Solids Concentrations of the MBR Permeates over the Black Liquor Carryover Testing Period (BL: Black Liquor Carryover Test; VDS: Volatile Dissolved Solids; TDS: Total Dissolved Solids; R1: Permeate of MBR 1; R2: Permeate of MBR 2; Time – 1st day: August 2, 2001)

The dissolved solids concentrations of the permeates were not greatly affected by the simulated black liquor carryover (Figure 5.20). A slight increase of dissolved solids concentrations was observed during the black liquor carryover tests, as indicated for BL 3 and BL 4. Thereafter, the solids concentrations returned to normal levels. Since the ability of a membrane bioreactor to remove non-biodegradable dissolved solids is poor (Ragona, 1998), the low impact on permeate dissolved solids concentrations is probably because black liquor carryover mostly increased the suspended solids concentrations of the condensate, not the dissolved solids concentration.

The flux of the membranes decreased more rapidly with the higher solid concentrations of condensate with black liquor carryover and the membrane would need more frequent cleaning if the black liquor carryover continued (See Appendix 6 and Section 5.7).

5.5.5 MLVSS Concentrations

Black liquor is a complex mixture of materials and contains many contaminants that may exert toxic effects on a mixed microbial culture. The MLVSS concentrations, as shown in Figure 5.21, slightly declined for both MBRs during the period of the black liquor carryover tests. Similarly, the observed growth yields of the MBRs also decreased during the period of black liquor carryover tests (for R1 decreased from 0.0254 to 0.0241, and for R2 decreased from 0.026 to 0.024). However, the effect of black liquor on the growth yield of biomass was not clearly observed and needs further study to be clarified.

Condensate used during black liquor carryover tests was collected from Howe Sound Pulp and Paper Ltd. (Port Mellon, BC, Canada). Therefore, two MBRs were acclimatized to the new condensate for two weeks. Steady state operation was assumed to have been reached because stable MLVSS concentrations and 95% methanol removal efficiencies were observed. The MLVSS concentration profiles during the steady state (day 0 to 15) are shown in Figure 5. 21.

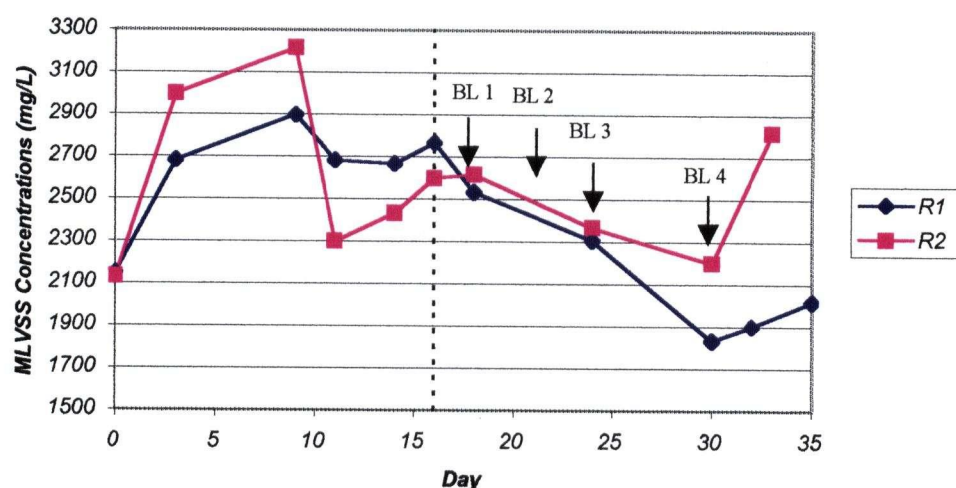


Figure 5.21 MLVSS Concentrations Profiles during Black Liquor Carryover Tests
(Time -1st day: July 16, 2001; Dashed Line: Start of the Black Liquor Carryover Test)

5.5.6 Summary

The performances of the MBRs weren't significantly affected and were able to degrade the excess COD and TOC during the first and second black liquor carryover tests. The third long-term black liquor carryover test started to show an inhibitory effect on the MBR performance, while the third short-term black liquor carryover test didn't seriously

influence the contaminant removal efficiencies of the MBR. The fourth black liquor carryover test had deleterious effects on the MBRs, both short-term and long-term. Methanol removal efficiency was greatly decreased by the simulated black liquor carryover and influenced TOC and COD removal efficiencies. For the short-term test, the MBR recovered relatively fast and the methanol concentration returned to normal levels after two batches (4 hours). Comparatively, the long-term test upset the MBR and the system recovered after two days.

The colour of the MBR permeates remained relatively constant throughout the period of the black liquor carryover tests. The excess colour resulted from black liquor carryover was mostly removed from the membrane filters and only increased the true colour of permeate from 250 to 400 A.P.H.A.

The MBRs removed all of the suspended solids, but their ability to remove non-biodegradable dissolved solids was poor. During the black liquor carryover tests, a slight increase of the dissolved solids concentrations of the permeate was observed. However, the flux of the membrane decreased more rapidly (discussed in more detail in section 5.7) and the membrane would need more frequent cleaning if the black liquor carryover continued.

The observed growth yield and MLVSS concentrations slightly declined for both MBRs during the period of the black liquor carryover tests. However, the effect of black liquor on the growth yield of biomass was not clearly observed and needs further study to be clarified.

5.6 Mill Shutdown Test

This test was designed to simulate a shutdown of the mill operation, which usually lasts 7 to 10 days. For ten days, the feeding, heating systems, and pH controller of the MBR were turned off. The aeration and circulation rates through membrane were turned down to just maintain aerobic conditions in the reactor. Subsequently, the MBR was restarted gradually by controlling temperature and feed rate, as described thoroughly in section 4.2.4. Data are presented in Appendix 5 and summarized in section 5.6. Results are discussed in section 5.6.

5.6.1 pH and Temperature of MBR

Temperature and pH in the reactor were recorded on a daily basis and are shown in Table 5.6. About six hours after shutdown, the temperature in the reactor gradually decreased from 60 °C to 32 °C, slightly higher than room temperature.

Temperature fluctuated with room temperature, but was never under 30 °C (ambient temperature was 20 to 28 °C during the test). This is probably because the membrane reactor was situated in an insulated box and heat generated from circulation through the membrane unit increased the heat content of the system. The pH increased from 6.5 to 8.4 slowly, and remained at approximately 8.4 after the sixth day of the shutdown test. The increase of pH throughout the shutdown period was possibly due to the stripping of dissolved carbon dioxide.

Table 5.6 Temperature and pH Conditions in MBR during Mill Shutdown Test

Time	Temperature (°C)	pH
August 24, 2001 9:00	60	6.57
11:00	47	6.87
13:00	49	6.96
15:00	32	7.08
August 25, 2001 9:00	31	7.60
August 26, 2001 9:00	32	7.92
August 27, 2001 9:00	34	8.16
August 28, 2001 9:00	31	8.18
August 29, 2001 9:00	34	8.37
August 30, 2001 9:00	34	8.34
August 31, 2001 9:00	33	8.39
September 1, 2001 9:00	35	8.31
September 2, 2001 9:00	32	8.40

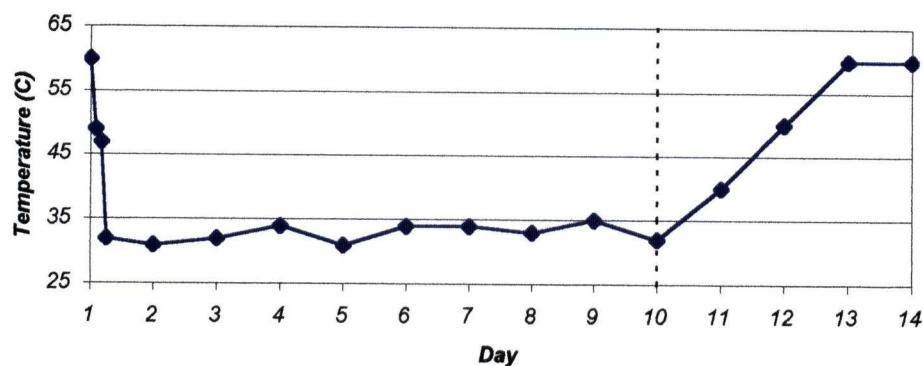


Figure 5.22 Temperature Profile during the Mill Shutdown Test

(Dashed Lined Indicates the End of the Mill Shutdown Period. At the Same Time, the MBRs were Returned to Normal Operating Conditions)

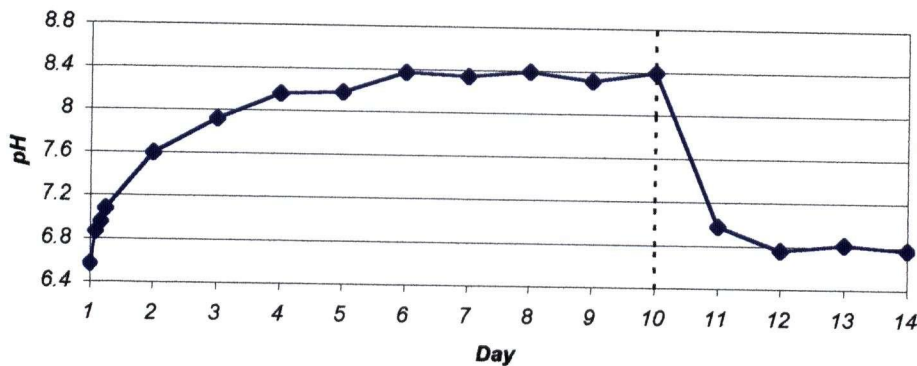


Figure 5.23 pH Profile during the Mill Shutdown Test

(Dashed Lined Indicates the End of the Mill Shutdown Period. At the Same Time, the MBRs were Returned to Normal Operating Conditions)

5.6.2 Methanol, TOC, and COD Removal

During the 10 days of the shutdown test, a batch test was performed every two days to monitor the activity of the system. A volume of 400 ml of kraft condensate was fed to the reactor and methanol, TOC, and COD concentrations were measured every 15 minutes for two hours. The methanol, TOC and COD utilization coefficient profiles are shown in Figure 5.24. It is obvious that the methanol, TOC and COD utilization coefficients decreased during the shutdown period. The methanol utilization coefficient decreased from 3 to 0.3; the TOC removal coefficient dropped from 1.34 to 0.1; and the COD removal coefficient declined from 4.3 to 1.3. However, the system recovered along with the increase of organic loading fairly well. It was shown that the MBR was capable of handling the long shutdown period and could recover in a short time to full capacity. No deleterious effects from the shutdown were observed. The methanol removal coefficient

recovered from 0.3 to 2.1; the TOC removal coefficient climbed back to 0.9; COD removal coefficient also increased to 3.9.

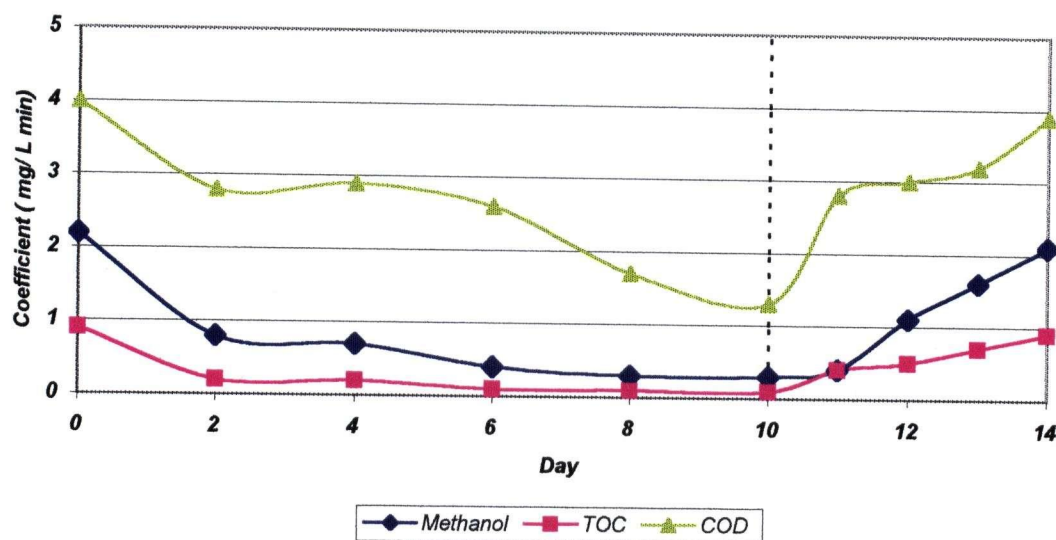


Figure 5.24 Methanol, TOC, and COD Utilization Coefficients Profiles over the Mill Shutdown Test Period (Dashed Lined Indicates the End of the Mill Shutdown Period.)

5.6.3 MLVSS concentrations

During the mill shutdown test, food was not available and microorganisms were forced to metabolize their own protoplasm without replacement. As a result, the MLVSS concentration in the membrane bioreactor decreased, as expected, from 3000 mg/L to 1200 mg/L over ten days (refer to Figure 5.25). After re-starting the feed, biomass MLVSS concentration increased back to 2400 mg/L, at a faster rate than the rate of decrease during the mill shutdown. No deleterious effects on the biomass from shutdown were observed. Poor settling ability commonly observed after shutdown in conventional

activated sludge system is not a concern with an MBR system because of the complete retention of biomass by the membrane unit.

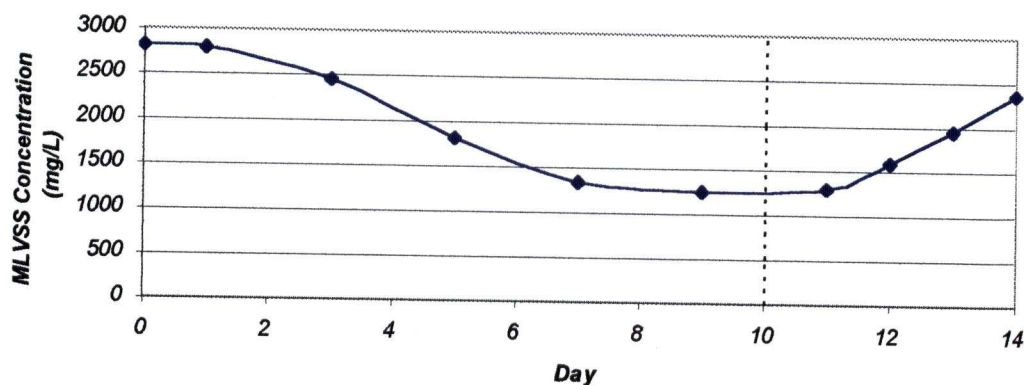


Figure 5.25 MLVSS Concentration in the MBR during the Mill Shutdown Test Period (Dashed Line Indicates That the Mill Shutdown Period, 10 days, finished. At the Same Time, the MBRs are Back to Normal Operating Conditions)

5.6.4 Summary

Methanol, TOC and COD utilization coefficients decreased during the shutdown period. However, the MBR system recovered along with an increase of organic loading fairly well, and it was obvious that MBR was capable of tolerating the long shutdown period and could recover in a short time to full capacity. No deleterious effects from shutdown were observed.

5.7 Membrane Performance

5.7.1 Initial Membrane Flux

Two 500-Angstrom Membralox T1-70 filters used in Bérubé's (2000) study were used during the period of steady state experimentation. The initial permeate flux of the membrane was measured by filtering tap water through the membrane at the same operating conditions as those during steady state experiment (refer to Table 4.2). The initial membrane flux was determined to be $160 \text{ L}/(\text{m}^2 \cdot \text{hr})$. Permeate flux gradually decreased and membrane cleaning was performed when flux dropped to $40 \text{ L}/(\text{m}^2 \cdot \text{hr})$.

Due to irreversible loss of permeate flux of one membrane, two new 500-Angstrom Membralox T1-70 filters with new casings were purchased and used for R2 during the periods of methanol shock loading tests, black liquor carryover tests, and mill shutdown test. R1 continuously used the previous membrane filter until the end of the experiment. The initial flux of the new membrane was determined to be $122 \text{ L}/(\text{m}^2 \cdot \text{hr})$. Permeate flux gradually decreased and membrane cleaning was performed when flux dropped to $40 \text{ L}/(\text{m}^2 \cdot \text{hr})$.

5.7.2 Permeate Flux

Membrane permeate flux was affected by a variety of factors. Since fouling was not the main interest of this study, this section simply presents permeates flux data and observations. The performances of the ultrafiltration membranes used in R1 and R2 during this study are illustrated in Figure 5.26 and 5.27 respectively.

Maximum flux always occurred immediately following a membrane cleaning, and decreased rapidly in the first few days to approximately 55 % of the maximum flux. Then, it declined slowly until another membrane cleaning was performed. The time required for a membrane cleaning varied between the different filters and throughout this study.

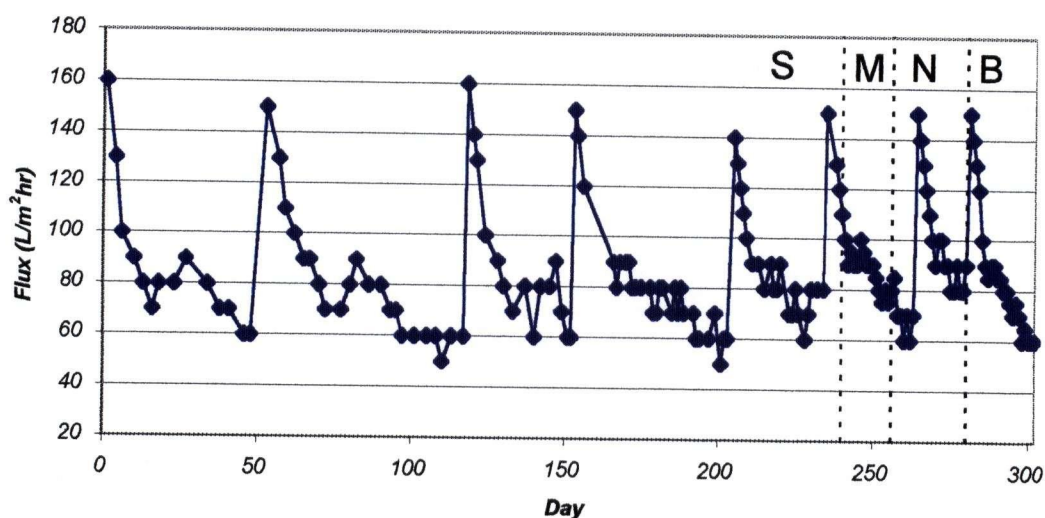


Figure 5.26 Permeate Flux of R1 (S: Steady-state; M: Methanol Shock Loading Tests; N: New New Combined Condensate from Howe Sound Pulp and Paper Ltd (Port Mellon, BC, Canada); B: Black Liquor Carryover Tests)

The membrane bioreactor R1 was capable of operating for up to 65 days without cleaning. During the black liquor carryover test, R1 didn't require the membrane cleaning even though the solids content of feed was 2 to 4 times higher than usual. The decrease rate of permeate flux during the period of black liquor carryover tests is slightly higher than that under normal operating conditions, but became stable after the tests were completed.

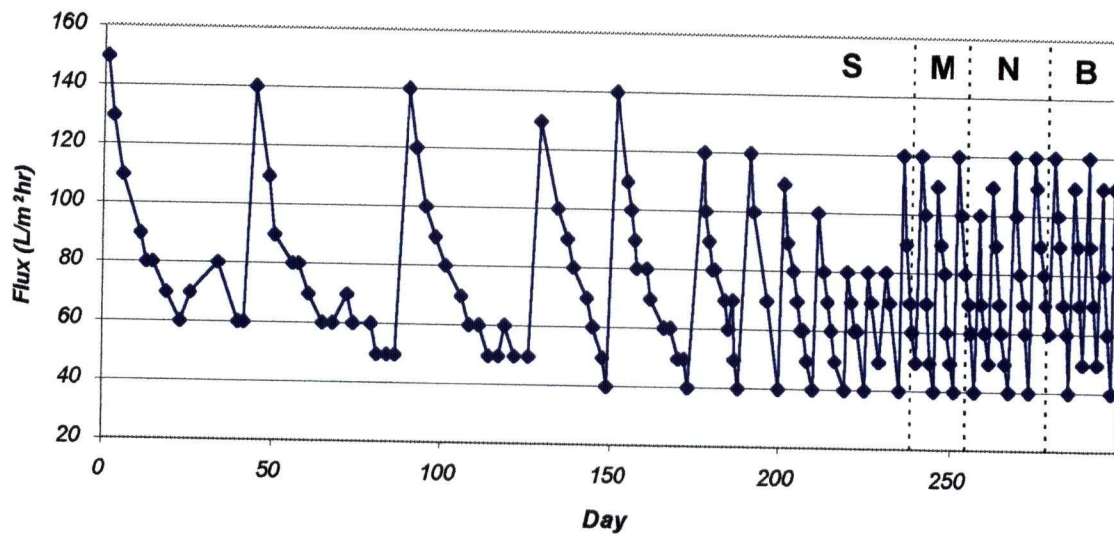


Figure 5.27 Permeate Flux of R2 (S: Steady-state; M: Methanol Shock Loading Tests; N: New Combined Condensate from Howe Sound Pulp and Paper Ltd (Port Mellon, BC, Canada); B: Black Liquor Carryover Tests)

In the beginning of the steady state, the membrane bioreactor R2 was capable of operating for up to 45 days without cleaning. Irreversible loss of permeate flux was observed on May 2001. Therefore, R2 was replaced with the new membrane filter and casing. The filter is the same configuration as the old one, except there is no stainless steel fitting on both ends. The new casing is only different on the part of membrane seal system. The minor difference should not cause any significant difference on membrane performance (Personal communication, Rishi Sondhi, 2001, U.S. Filter, Deland, Florida).

After R2 was replaced with the new membrane unit, the MBR 2 system required much more frequent cleaning than before. As shown in Figure 5.27, the membrane flux dropped more rapidly and it required cleaning every 4 to 6 days. To clarify whether the high

cleaning frequency was caused by the different mixed liquors of the two MBRs, the membrane unit of R2 was connected with reactor 1 for three days after cleaning. However, similar rapid flux decrease and low membrane flux were observed. Therefore, it was concluded that the lower membrane flux resulted from the nature of the new membrane unit, not from the different mixed liquors in the MBR reactors. More investigation is required to identify the causes of the membrane fouling.

Chapter 6 Conclusions and Recommendations

6.1 Conclusions

Steady State Experiment

The results of the present study during the steady state experiments are summarized and compared with Bérubé's (2000) results, as shown in Table 6.1.

Table 6.1 Summary of the results of the steady state experiment of the present study and Bérubé's (2000) research

	Methanol Removal Efficiency (%)	Specific Methanol Utilization Coefficient (day ⁻¹)	TOC Removal Efficiency (%)	Specific TOC Utilization Coefficient (day ⁻¹)	MLVSS Concentration (mg / L)	Operating Conditions		
						SRT (days)	HRT (hrs)	Methanol Concentration (mg / L)
Present Study	95	R1: 1.03 R2: 1.47	64	R1: 0.51 R2: 0.74	R1: 3000 R2: 2500	38	9	1200
Bérubé (2000)	99	0.59	93	0.66	2500	20	18	900

The major conclusions from the experiment were as follows.

1. The MBRs exhibited stable removal of the main contaminants, methanol and organic components expressed as TOC. The difference between TOC removal efficiencies of

the present study and Bérubé's research (2000) was due to the different calculation methods used for removal efficiency, as explained in section 5.3.1.

2. With a long SRT (38 days), the MBRs exhibited a low observed growth yield, 0.0347 for R1 and 0.0254 for R2. Low growth yield is considered an advantage of the process because of the associated low biosolids management cost.
3. The MBR was operated as long as 65 days without membrane cleaning. However, unknown causes resulted in the irreversible fouling of the membrane unit for R2 and may be a potential problem for MBR operation.

Methanol Shock Loading Tests

The MBRs were subjected to three methanol shock loading tests. By adding methanol into the feed condensate, the methanol concentrations of the feed condensate were increased by 1.5, 2, and 2.5 times. R1 was subjected to four shock loadings to investigate long-term effects, and R2 was subjected to one shock loading to identify short-term effects. Major findings of the methanol shock loading tests are as follows.

1. The MBRs were reasonably stable and able to achieve the same removal efficiency when the load was increased by 1.5 and 2 times instantaneously. When the feed strength was increased by a factor of 2.5, the MBRs showed distinct signs of

overload. However, R1 recovered about four hours after the short-term shock loadings, and R2 recovered two days after the long-term shock loadings.

2. An overload of methanol seemed to disturb the biomass and the colour of the permeate increased slightly after the methanol shock loading test in which methanol concentration was increased by 2.5 times.
3. Excess methanol from the methanol shock loading tests increased slightly the growth yields and the MLVSS concentrations in the MBRs.

Black Liquor Carryover Tests

The effects of simulated black liquor spills on a high temperature MBR treating kraft condensate was investigated by four black liquor carryover tests. Concentrations of 4 mL, 6 mL, 8 mL and 16 mL black liquor per litre kraft condensate were chosen as the intensities of the black liquor carryover tests of the present study. The reactor was subjected to four shock loadings to investigate long-term effects, and one shock loading to identify short-term effects. Major conclusions are as follows.

1. The performances of MBRs weren't significantly affected, as the systems were able to degrade the excess COD and TOC during black liquor carryover tests with 4 mL and 6 mL black liquor per litre evaporator condensate. The long-term black liquor carryover test with 8 mL black liquor per litre evaporator condensate started to show

an inhibitory effect on the MBR performance. The short-term black liquor carryover test at the same black liquor concentration didn't seriously influence the contaminant removal efficiencies of the MBR.

2. The black liquor carryover test with 16 mL black liquor per litre evaporator condensate resulted in deleterious effects on the MBRs, both short-term and long-term. Methanol removal efficiency was greatly decreased by the black liquor carryover and influenced TOC and COD removal efficiencies. For the short-term test, the MBR recovered relatively fast and the methanol concentration returned to normal levels after two batch cycles (4 hours). Comparatively, the long-term test upset the MBR and the system recovered after two days.
3. The colour of the MBRs' permeates remained relatively constant throughout the period of the black liquor carryover tests. The excess colour resulted from black liquor carryover was mostly removed by the membrane filters and only increased true colour of permeate from 250 to 400 A.P.H.A.
4. A slight increase in the dissolved solids concentrations of the permeate during the black liquor carryover tests was observed. The MBRs removed all of the suspended solids, but their ability to remove non-biodegradable dissolved solids was poor.
5. The permeate flux of the membrane decreased more rapidly and the membrane would need more frequent cleaning if the black liquor carryover continued.

6. The observed growth yield and MLVSS concentrations declined slightly for both MBRs during the period of the black liquor carryover tests. However, the effect of black liquor on the growth yield of biomass was not clearly observed and needs further study to be clarified.

Mill Shutdown Tests

Methanol, TOC, and COD utilization coefficients decreased during the shutdown period. However, the MBR system recovered along with an increase of feed loading fairly well, and it was obvious that MBR was capable of handling the 10-day shutdown period and was able to recover in a short time to full capacity. No deleterious effects from a 10-day shutdown were observed.

6.2 Recommendations

With limited time, the present research project could only discover the tip of the iceberg regarding the effects of transient loads on the MBR performance. There were new questions generated and waiting to be answered. The following are possible areas of further research to complete our understanding of high temperature MBR treating kraft mill condensate.

1. The effects of temperature variations on the high temperature MBR were not investigated and are important to improve our understanding of the stability of the high temperature MBR system treating kraft condensate.
2. The performance of the membrane was not the focus of the present study. However, irreversible fouling was observed for one of the membrane unit and may be a potential problem for the membrane bioreactor. Further research is required to optimize the MBR operation with respect to the membrane performance.
3. The purpose of the present study was to examine the treatment of kraft evaporator condensate by high temperature MBR. To be more economically attractive, further research is required to investigate the feasibility of a high temperature MBR treating kraft combined condensate, both the evaporator and digester areas. Especially, Dr. Barton suggested that turpentine shock loading would be the one of main interests of the study on the treatment system of kraft combined condensate treatment (personal communication, Doug Barton, 2001, NCASI).
4. MLVSS concentration of MBR commonly ranges from 10,000 to 30,000 mg/L at various SRT. During the present study, low MLVSS concentrations were observed and could be a potential factor causing unstable MBR operation. Further research is needed to identify the causes and the effects of the low MLVSS concentrations on the MBR performance.

5. Shock loads are often divided into two ways: either short-term shock loads which only last a few hours, or long-term changes of days or weeks duration before returning to the original operating conditions (Nachaiyasit and Stuckey, 1997a). During the present study, the long-term shock loads only lasted approximately one HRT. To further investigate the effects of long-term shock loadings on the MBR performance, longer shock loadings should be applied to system.

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Appendix 1 Characteristics of Kraft Condensate

During the period of steady state testing and the methanol shock loading tests, the evaporator condensate was shipped from the Western Pulp Limited Partnership bleached kraft mill (Squamish, BC, Canada) to UBC. The characteristics of the evaporator condensate used for the present study are presented in Table A1 – 1.

Combined condensate was collected from Howe Sound Pulp and Paper Limited Partnership (Port Mellon, BC, Canada) during the black liquor spill tests and mill shutdown test. The characteristics of the combined condensate are presented in table A1 – 2.

Notably, received condensate that had conductivity greater than 800 μS was discarded and not considered as representative samples.

Table A1 - 1 Characteristics of Evaporator Condensate from Western Pulp Ltd.

	Conductivity (μ S)	pH	Methanol (mg/L)	TOC (mg C/L)	TOC filtered (mg C/L)	TOC solid(%)	Methanol as TOC(%)
13-Jul-00	175	6.5	487	273	252	7.7	66.9
19-Jul-00	195	6.5	324	290	261	10.0	41.9
2-Aug-00	150	7	393	273	256	6.2	54.0
9-Aug-00	500	9	455	373	352	5.6	45.7
30-Aug-00	385	6	458	468	417	10.9	36.7
14-Sep-00	270	6	529	434	413	4.8	45.7
5-Oct-200	260	6	456	418	380	9.1	40.9
12-Oct-00	290	8.5	433	444	438	1.4	36.6
18-Oct-00	320	8.5	457	513	464	9.6	33.4
25-Oct-00	260	8	936	464	458	1.3	75.6
2-Nov-00	540	8.47	319	297	278	6.4	40.3
9-Nov-00	135	7.5	399	350	348	0.6	42.8
15-Nov-00	170	7.88	363	302	281	7.0	45.1
23-Nov-00	145	7.39	427	360	342	5.0	44.5
6-Dec-00	130	7.47	374	359	338	5.8	39.1
13-Dec-00	385	7.16	441	400	378	5.5	41.3
20-Dec-00	360	7.14	508	294	273	7.1	64.8
10-Jan-01	580	7.86	359	440	392	10.9	30.6
17-Jan-01	580	7.80	373	416	400	3.8	33.6
24-Jan-01	600	7.43	319	371	301	18.9	32.2
31-Jan-01	590	7.42	341	364	259	28.8	35.1
7-Feb-01	490	7.89	319	348	240	31.0	34.4
14-Feb-01	480	7.99	317	276	222	19.6	43.1
28-Feb-01	590	8.1	399	342	310	9.4	43.8
8-Mar-01	680	8.7	359	414	402	2.9	32.5
14-Mar-01	720	8.4	378	432	408	5.6	32.8
4-Apr-01	500	8.5	324	336	330	1.8	36.2
11-Apr-01	630	8.94	325	348	332	4.6	35.0
18-Apr-01	210	7.42	225	199	182	8.5	42.4
25-Apr-01	210	7.49	213	207	183	11.6	38.6
2-May-01	380	7.91	317	212	196	7.5	56.1
9-May-01	395	7.91	277	180	152	15.6	57.7
16-May-01	430	7.94	321	240	208	13.3	50.2
23-May-01	255	8.17	309	164	148	9.8	70.7
30-May-01	395	8.17	347	248	208	16.1	52.5
6-Jun-01	255	8.14	243	160	148	7.5	57.0
13-Jun-01	370	8.34	304	204	188	7.8	55.9
20-Jun-01	470	7.93	335	244	224	8.2	51.5
27-Jun-01	370	8.01	359	248	212	14.5	54.3
Average	381	7.7	380	326	297	9.3	45.4
+/- (10%)	44	0.2	31	25	24	2	3.0

Table A1 - 2 Characteristics of Combined Condensate from Howe Sound Pulp and Paper Ltd.

	Conductivity (μ S)	pH	Methanol (mg/L)	TOC (mg C/L)	TOC filtered (mg C/L)	TOC solid(%)	Methanol as TOC(%)	COD (mg O ₂ /L)
1	500	8.6	4920	2085	1980	5	88	9310
2	500	8.4	5080	1985	1880	5	96	9180
3	450	8.2	4860	2185	1910	13	83	9420
Average	483	8.4	4953	2085	1923	8	89	9303
+/- (10%)	27	0.2	108	95	49	4.1	6	114

Appendix 2 Data Collected During Steady State Experiment

Appendix 2 contains the data collected during steady state experiment. Results from batch tests monitoring removal kinetics of methanol and total organic carbon (TOC) are presented in Table A2 – 1 to A2 – 12 for Reactor 1, and Table A2 – 13 to Table A2- 24 for reactor 2. For these tables, the parameter K is the zero order coefficient for the biological removal of contaminant (mg/L·min). The parameter Co is the initial concentration in the MBR and the parameter Ce is the final TOC concentration in the MBR, derived from the second zero order removal coefficient. The R^2 value is the coefficient of determination for linear regression.

The calculations for observed growth yields of R1 and R2 are presented in Table A2 – 25 and Table A2 – 26.

Results from methanol removal efficiency tests are summarized in Table A2 – 27.

The incidents happened during the steady state experiment are summarized in Table A2 – 28.

Contaminant Removal - Steady State - Reactor 1

Table A2 - 1 March 28, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	227.6	166	
30	186	152	
45	172.1	122	
60	123	103	
75	32.4	94	
90	0	87	
Co (Ce)	284.2	190.7	(71.1)
K	3	1.47	0.53
R ²	0.92	0.958	0.995

Table A2 - 4 May 1, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	237.6	152	
30	163.2	118	
45	148.7	92	
60	114.3	81	
75	94.5	78	
90	33.2	73	
Co (Ce)	258.2	170.5	(64.9)
K	2.4	1.59	0.27
R ²	0.953	0.955	0.98

Table A2 - 2 April 13, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	213.3	158	
30	186.5	138	
45	132.7	126	
60	68.9	105	
75	26.5	93	
90	0	86	
Co (Ce)	272.9	174.5	(66.2)
K	3.3	1.14	0.63
R ²	0.985	0.99	0.977

Table A2 - 5 May 8, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	272.2	188	
30	225.9	154	
45	209.5	150	
60	174.4	123	
75	152.9	109	
90	111.5	103	
Co (Ce)	296.8	203.5	(81.3)
K	2	1.33	0.67
R ²	0.986	0.929	0.95

Table A2 - 3 April 18, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	233.9	144	
30	133.1	124	
45	115.2	98	
60	61.2	79	
75	39.3	73	
90	12.5	68	
Co (Ce)	243.4	166.5	(56.4)
K	2.7	1.47	0.37
R ²	0.926	0.997	0.997

Table A2 - 6 May 12, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	213.3	144	
30	188.9	130	
45	167.7	102	
60	132.2	83	
75	105.3	75	
90	68.8	70	
Co (Ce)	246.9	167.5	(56.9)
K	1.9	1.41	0.43
R ²	0.993	0.986	0.983

Contaminant Removal - Steady State - Reactor 1 - Con't

Table A2 - 7 May 22, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	219.8	152	
30	190.7	136	
45	128.9	112	
60	52.9	95	
75	22.1	88	
90	3.2	79	
Co (Ce)	269.4	172.5	(63.7)
K	3.2	1.3	0.53
R ²	0.965	0.994	0.995

Table A2 - 10 June 10, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	213.8	148	
30	182.7	128	
45	139.8	106	
60	107.6	77	
75	37	71	
90	0	66	
Co (Ce)	267.3	173.5	(54.4)
K	2.9	1.57	0.37
R ²	0.985	0.992	0.997

Table A2 - 8 May 29, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	207.6	144	
30	151.5	111	
45	101.1	96	
60	50.3	76	
75	0	72	
90	0	65	
Co (Ce)	258.2	161.5	(54.1)
K	3.5	1.46	0.37
R ²	0.999	0.972	0.976

Table A2 - 11 June 14, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	214.4	145	
30	162.8	125	
45	122.4	110	
60	93.5	97	
75	46.8	89	
90	3.3	77	
Co (Ce)	250.4	159	(57.3)
K	2.7	1.06	0.67
R ²	0.995	0.99	0.987

Table A2 - 9 June 4, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	207.6	143	
30	178.5	123	
45	133.5	107	
60	84.3	89	
75	37.6	80	
90	0	73	
Co (Ce)	257.9	160	(57.1)
K	2.9	1.19	0.53
R ²	0.996	0.998	0.995

Table A2 - 12 June 24, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	215.3	145	
30	173.8	134	
45	124.9	113	
60	73.4	93	
75	42.5	87	
90	0	77	
Co (Ce)	257.2	165.5	(59.4)
K	2.9	1.18	0.53
R ²	0.996	0.984	0.98

Contaminant Removal - Steady State - Reactor 2

Table A2 - 13 March 28, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	190.8	138	
30	161.9	108	
45	142.1	100	
60	113.5	73	
75	75.4	69	
90	40.2	63	
Co (Ce)	224.8	155.5	(53.3)
K	2	1.35	0.33
R ²	0.989	0.96	0.987

Table A2 - 16 May 1, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	226	144	
30	190.5	118	
45	148.7	98	
60	112.7	85	
75	93.2	78	
90	31.5	69	
Co (Ce)	263.8	160.5	(53.7)
K	2.5	1.3	0.53
R ²	0.986	0.979	0.995

Table A2 - 14 April 14, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	207.2	148	
30	163.8	138	
45	148.2	106	
60	114	95	
75	94.6	88	
90	22.7	79	
Co (Ce)	241.5	169.5	(63.7)
K	2.2	1.27	0.53
R ²	0.9535	0.952	0.995

Table A2 - 17 May 8, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	238.9	163	
30	204.6	146	
45	168.8	129	
60	120.3	107	
75	85.6	94	
90	54.3	87	
Co (Ce)	278.3	182.5	(65.6)
K	2.5	1.23	0.67
R ²	0.997	0.996	0.971

Table A2 - 15 April 23, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	179.5	134	
30	158.4	104	
45	121.6	86	
60	92.8	76	
75	54.3	70	
90	4.5	63	
Co (Ce)	223.5	140	(50.6)
K	2.3	1.2	0.43
R ²	0.986	0.9481	0.998

Table A2 - 18 May 12, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	213.4	134	
30	174.3	120	
45	132.5	92	
60	88.4	76	
75	41.1	68	
90	0	63	
Co (Ce)	259.4	156	(49.9)
K	2.9	1.35	0.43
R ²	0.999	0.983	0.983

Contaminant Removal - Steady State - Reactor 2 - Con't

Table A2 - 19 May 22, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	197.1	150	
30	178.2	129	
45	127.4	114	
60	82.3	95	
75	36.9	87	
90	0	80	
Co (Ce)	249.1	167	(64.8)
K	2.8	1.2	0.5
R ²	0.991	0.999	0.999

Table A2 - 22 June 10, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	233.6	157	
30	199.4	139	
45	144.8	119	
60	120.4	103	
75	79	93	
90	37.6	84	
Co (Ce)	272.4	175	(65.3)
K	2.6	1.21	0.63
R ²	0.994	0.998	0.999

Table A2 - 20 May 29, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	199.5	130	
30	164.5	116	
45	125.6	102	
60	96.3	81	
75	58.8	74	
90	24.6	64	
Co (Ce)	233.6	147.5	(47.1)
K	2.3	1.07	0.57
R ²	0.999	0.989	0.99

Table A2 - 23 June 14, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	214.4	143	
30	188.3	127	
45	143.5	111	
60	122.2	89	
75	94.5	84	
90	52.3	74	
Co (Ce)	247.2	162	(59.8)
K	2.1	1.19	0.5
R ²	0.991	0.9932	0.964

Table A2 - 21 June 4, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	219.5	140	
30	187.4	123	
45	127.8	109	
60	105.7	82	
75	74.2	76	
90	38.1	68	
Co (Ce)	252.3	160.5	(53.9)
K	2.4	1.25	0.47
R ²	0.985	0.979	0.993

Table A2 - 24 June 24, 2001

Time (min)	Methanol (mg/L)	TOC (mg/L)	
15	229.3	149	
30	190.4	131	
45	154.3	118	
60	111.2	95	
75	82.4	88	
90	41.7	77	
Co (Ce)	265.4	167	(59.7)
K	2.5	1.17	0.6
R ²	0.998	0.989	131.7

Table A2 - 25 Growth Yield of Reactor 1 During Period of Steady State Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
28-Mar-01	0	457	5320	261	0	0
29-Mar-01	1	418	5320	261	5016	261
30-Mar-01	2	438	3593	176	10272	437
31-Mar-01	3	471	3593	176	15924	613
2-Apr-01	5	518	3593	176	28356	965
12-Apr-01	15	486	4120	202	86676	2984
13-Apr-01	16	451	5398	265	92088	3248
14-Apr-01	17	492	5398	265	97992	3513
16-Apr-01	18	468	5661	277	103608	3790
17-Apr-01	19	468	4622	226	109224	4017
18-Apr-01	20	386	4622	226	113856	4243
19-Apr-01	21	372	4622	226	118320	4470
20-Apr-01	22	394	4622	226	123048	4696
23-Apr-01	23	414	4083	200	128016	4896
24-Apr-01	24	448	4083	200	133392	5096
25-Apr-01	25	442	5267	258	138696	5354
26-Apr-01	26	503	5267	258	144732	5612
27-Apr-01	27	451	5267	258	150144	5870
30-Apr-01	30	395	5267	258	164364	6645
1-May-01	31	350	5267	258	168564	6903
2-May-01	32	488	5267	258	174420	7161
3-May-01	33	476	4967	243	180132	7404
4-May-01	34	498	4967	243	186108	7648
7-May-01	37	462	4700	230	202740	8338
8-May-01	38	470	2472	121	208380	8460
9-May-01	39	478	2472	121	214116	8581
12-May-01	42	486	3333	163	231612	9071
14-May-01	44	447	3333	163	242340	9397
16-May-01	46	429	3489	171	252636	9739
17-May-01	47	473	3489	171	258312	9910
18-May-01	48	439	3455	169	263580	10079
20-May-01	50	488	3455	169	275292	10418
21-May-01	51	477	3455	169	281016	10587
22-May-01	52	467	4044	198	286620	10786
23-May-01	53	491	4044	198	292512	10984
24-May-01	54	479	4044	198	298260	11182
26-May-01	56	470	3517	172	309540	11527
27-May-01	57	483	3517	172	315336	11699
29-May-01	59	490	3517	172	327096	12044
30-May-01	60	428	3517	172	332232	12216
31-May-01	61	458	3617	177	337728	12393
1-Jun-01	62	465	3617	177	343308	12570
4-Jun-01	65	492	3300	162	361020	13055
5-Jun-01	66	450	3300	162	366420	13217
6-Jun-01	67	494	3300	162	372348	13379
7-Jun-01	68	429	3167	155	377496	13534
8-Jun-01	69	493	3167	155	383412	13689
10-Jun-01	71	459	2983	146	394428	13982
11-Jun-01	72	443	2983	146	399744	14128
12-Jun-01	73	430	2983	146	404904	14274
14-Jun-01	74	446	3306	162	410256	14436
16-Jun-01	76	434	3306	162	420672	14760
17-Jun-01	77	435	3283	161	425892	14921
20-Jun-01	80	447	2800	137	441984	15332
					Growth Yield	0.0347

*Measured MLVSS Value in Bold.

Table A2 - 26 Growth Yield of Reactor 2 During Period of Steady State Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
28-Mar-01	0	476	2567	133	0	0
1-Apr-01	4	415	2305	120	19920	479
2-Apr-01	5	457	2305	120	25404	599
3-Apr-01	6	425	2420	126	30504	725
4-Apr-01	7	465	2420	126	36084	851
7-Apr-01	10	412	2420	126	50916	1229
8-Apr-01	11	473	2420	126	56592	1354
12-Apr-01	15	483	2420	126	79776	1858
14-Apr-01	17	447	1842	96	90504	2049
16-Apr-01	19	483	2611	136	102096	2321
18-Apr-01	21	465	2611	136	113256	2592
19-Apr-01	22	484	2611	136	119064	2728
23-Apr-01	26	458	2733	142	141048	3297
24-Apr-01	27	448	3067	159	146424	3456
25-Apr-01	28	423	3067	159	151500	3616
26-Apr-01	29	484	3067	159	157308	3775
27-Apr-01	30	473	3067	159	162984	3935
30-Apr-01	33	472	3067	159	179976	4413
1-May-01	34	455	3067	159	185436	4572
2-May-01	35	487	3067	159	191280	4732
3-May-01	36	496	2264	118	197232	4850
4-May-01	37	483	2264	118	203028	4967
7-May-01	40	460	2555	133	219588	5366
8-May-01	41	462	2555	133	225132	5499
12-May-01	45	437	2555	133	246108	6030
16-May-01	49	464	3206	167	268380	6697
17-May-01	50	426	3206	167	273492	6864
18-May-01	51	461	3206	167	279024	7031
20-May-01	53	433	3206	167	289416	7364
21-May-01	54	432	3206	167	294600	7531
22-May-01	55	455	2833	147	300060	7678
23-May-01	56	479	2833	147	305808	7825
24-May-01	57	480	2833	147	311568	7973
26-May-01	59	418	2633	137	321600	8246
27-May-01	60	482	2633	137	327384	8383
29-May-01	62	454	2754	143	338280	8670
30-May-01	63	439	2754	143	343548	8813
31-May-01	64	519	2900	151	349776	8964
1-Jun-01	65	486	2900	151	355608	9115
4-Jun-01	68	451	2767	144	371844	9546
5-Jun-01	69	497	2767	144	377808	9690
6-Jun-01	70	489	2767	144	383676	9834
7-Jun-01	71	487	3000	156	389520	9990
8-Jun-01	72	283	3000	156	392916	10146
10-Jun-01	74	468	2617	136	404148	10418
11-Jun-01	75	499	2617	136	410136	10554
12-Jun-01	76	448	2617	136	415512	10690
14-Jun-01	78	470	2472	129	426792	10947
16-Jun-01	80	478	2472	129	438264	11205
17-Jun-01	81	439	2472	129	443532	11333
20-Jun-01	84	477	2283	119	460704	11689
					Growth Yield	0.0254

*Measured MLVSS Value in Bold.

Table A2 - 27 Methanol Removal During the Period of Steady State Tests

Reactor 1						Reactor 2					
Date	Day #	Methanol Removal Efficiency (%)	Influent Methanol Concentration (mg/L Condensate)	Initial Methanol Concentration (mg/L mixed liquor)	Average Effluent Concentration (mg/L mixed liquor)	Date	Day #	Methanol Removal Efficiency (%)	Influent Methanol Concentration (mg/L Condensate)	Initial Methanol Concentration (mg/L mixed liquor)	Average Effluent Concentration (mg/L mixed liquor)
26-Oct-00	1	95	1186	263.6	13.2	26-Oct-00	1	96	1186	263.6	10.5
29-Oct-00	4	99	1156	256.9	2.6	28-Oct-00	3	98	1147	254.9	5.1
31-Oct-00	6	99	1288	286.2	2.9	31-Oct-00	6	97	1288	286.2	8.6
04-Nov-00	10	92	1255	278.9	22.3	05-Nov-00	11	97	1238	275.1	8.3
07-Nov-00	13	96	1175	261.1	10.4	07-Nov-00	13	78	1175	261.1	57.4
10-Nov-00	16	96	1097	243.8	9.8	09-Nov-00	15	93	1101	244.7	17.1
12-Nov-00	18	97	1154	256.4	7.7	13-Nov-00	19	96	1161	258.0	10.3
17-Nov-00	23	99	1247	277.1	2.8	17-Nov-00	23	95	1247	277.1	13.9
21-Nov-00	27	98	1124	249.8	5.0	20-Nov-00	26	98	1138	252.9	5.1
28-Nov-00	34	97	1146	254.7	7.6	28-Nov-00	34	99	1146	254.7	2.5
02-Dec-00	38	96	1268	281.8	11.3	04-Dec-00	40	96	1278	284.0	11.4
05-Dec-00	41	93	1254	278.7	19.5	06-Dec-00	42	96	1244	276.4	11.1
10-Dec-00	46	80	1168	259.6	51.9	09-Dec-00	45	95	1214	269.8	13.5
12-Dec-00	48	94	1174	260.9	15.7	13-Dec-00	49	97	1177	261.6	7.8
17-Dec-00	53	93	1169	259.8	18.2	15-Dec-00	51	96	1194	265.3	10.6
21-Dec-00	57	94	1236	274.7	16.5	20-Dec-00	56	98	1210	268.9	5.4
23-Dec-00	59	95	1185	263.3	13.2	22-Dec-00	58	95	1180	262.2	13.1
26-Dec-00	62	95	1265	281.1	14.1	25-Dec-00	61	96	1243	276.2	11.0
29-Dec-00	65	98	1099	244.2	4.9	29-Dec-00	65	61	1099	244.2	95.2
31-Dec-00	67	99	1084	240.9	2.4	30-Dec-00	68	80	1433	318.4	63.7
03-Jan-01	70	89	1568	348.4	38.3	05-Jan-01	72	95	1244	276.4	13.8
05-Jan-01	72	96	1244	276.4	11.1	07-Jan-01	74	96	1227	272.7	10.9
10-Jan-01	77	84	1183	262.9	42.1	12-Jan-01	79	94	1166	259.1	15.5
13-Jan-01	80	99	1172	260.4	2.6	14-Jan-01	81	97	1165	258.9	7.8
15-Jan-01	82	98	1212	269.3	5.4	17-Jan-01	84	98	1216	270.2	5.4
19-Jan-01	86	98	1208	268.4	5.4	19-Jan-01	86	96	1208	268.4	10.7
23-Jan-01	90	99	1163	258.4	2.6	23-Jan-01	90	68	1163	258.4	82.7
26-Jan-01	93	97	1175	261.1	7.8	25-Jan-01	92	92	1187	263.8	21.1
28-Jan-01	95	95	1224	272.0	13.6	28-Jan-01	95	95	1224	272.0	13.6
30-Jan-01	97	97	1263	280.7	8.4	31-Jan-01	98	97	1270	282.2	8.5
03-Feb-01	101	86	1255	278.9	39.0	03-Feb-01	101	98	1255	278.9	5.6
07-Feb-01	105	99	1236	274.7	2.7	08-Feb-01	106	99	1243	276.2	2.8
10-Feb-01	108	99	1218	270.7	2.7	10-Feb-01	108	99	1218	270.7	2.7
12-Feb-01	110	96	1186	263.6	10.5	13-Feb-01	111	98	1186	263.6	5.3
15-Feb-01	113	91	1202	267.1	24.0	16-Feb-01	114	95	1197	266.0	13.3
19-Feb-01	117	82	1254	278.7	50.2	19-Feb-01	117	96	1254	278.7	11.1
23-Feb-01	121	94	1232	273.8	16.4	21-Feb-01	119	97	1233	274.0	8.2
26-Feb-01	124	95	1174	260.9	13.0	23-Feb-01	122	98	1213	269.6	5.4
02-Mar-01	128	98	1154	256.4	5.1	27-Feb-01	126	93	1158	257.3	18.0
04-Mar-01	130	92	1136	252.4	20.2	03-Mar-01	129	78	1136	252.4	55.5
07-Mar-01	133	96	1216	270.2	10.8	08-Mar-01	134	95	1220	271.1	13.6
11-Mar-01	137	96	1200	266.7	10.7	11-Mar-01	137	93	1200	266.7	18.7
14-Mar-01	140	98	1233	274.0	5.5	13-Mar-01	139	95	1241	275.8	13.8
16-Mar-01	142	97	1254	278.7	8.4	17-Mar-01	143	90	1237	274.9	27.5
19-Mar-01	145	96	1155	256.7	10.3	19-Mar-01	145	96	1155	256.7	10.3
21-Mar-01	147	93	1123	249.6	17.5	22-Mar-01	148	98	1123	249.6	5.0
23-Mar-01	149	94	1012	224.9	13.5	23-Mar-01	149	97	1012	224.9	6.7
25-Mar-01	151	95	1279	284.2	14.2	25-Mar-01	151	90	1279	284.2	28.4
26-Mar-01	152	99	1158	257.3	2.6	29-Mar-01	155	95	1143	254.0	12.7
27-Mar-01	153	99	1074	238.7	2.4	30-Mar-01	156	97	1254	278.7	8.4
28-Mar-01	154	92	1132	251.6	20.1	31-Mar-01	157	97	1222	271.6	8.1
30-Mar-01	156	96	1254	278.7	11.1	01-Apr-01	158	94	1184	263.1	15.8
09-Apr-01	166	96	1086	241.3	9.7	04-Apr-01	161	89	1085	241.1	26.5
10-Apr-01	167	97	1228	272.9	8.2	05-Apr-01	162	92	1085	241.1	19.3
11-Apr-01	168	99	1198	266.2	2.7	09-Apr-01	166	99	1123	249.6	2.5
13-Apr-01	170	98	1165	258.9	5.2	11-Apr-01	168	97	1198	266.2	8.0
14-Apr-01	171	97	1124	249.8	7.5	13-Apr-01	170	98	1165	258.9	5.2
15-Apr-01	172	96	1095	243.3	9.7	15-Apr-01	172	94	1095	243.3	14.6
16-Apr-01	173	93	1152	256.0	17.9	16-Apr-01	173	93	1152	256.0	17.9
18-Apr-01	175	80	1124	249.8	50.0	20-Apr-01	177	87	1206	268.0	34.8
21-Apr-01	178	94	1006	223.6	13.4	21-Apr-01	178	93	1006	223.6	15.6
22-Apr-01	179	93	1266	281.3	19.7	22-Apr-01	179	88	1266	281.3	33.8
23-Apr-01	180	94	1241	275.8	16.5	23-Apr-01	180	94	1241	275.8	16.5
24-Apr-01	181	95	1186	263.6	13.2	24-Apr-01	181	97	1186	263.6	7.9
25-Apr-01	182	95	1162	258.2	12.9	27-Apr-01	184	92	1162	258.2	20.7
28-Apr-01	185	98	1088	241.8	4.8	28-Apr-01	185	91	1088	241.8	21.8
29-Apr-01	186	99	1278	284.0	2.8	29-Apr-01	186	97	1278	284.0	8.5
30-Apr-01	187	89	1156	256.9	28.3	30-Apr-01	187	97	1156	256.9	7.7
01-May-01	188	96	1100	244.4	9.8	01-May-01	188	99	1100	244.4	2.4
02-May-01	189	84	1233	274.0	43.8	04-May-01	191	99	1243	276.2	2.8
05-May-01	192	99	1167	259.3	2.6	05-May-01	192	96	1168	259.5	10.4
06-May-01	193	98	1336	296.9	5.9	09-May-01	196	95	1125	250.0	12.5
07-May-01	194	98	1248	277.3	5.5	13-May-01	200	99	1314	292.0	2.9
10-May-01	197	99	1111	246.9	2.5	14-May-01	201	97	1256	279.1	8.4
12-May-01	199	97	1322	293.8	8.8	15-May-01	202	93	1252	278.3	19.5
14-May-01	201	95	1256	279.1	14.0	17-May-01	204	91	1233	274.0	24.7
15-May-01	202	97	1256	279.1	8.4	18-May-01	205	86	1142	253.8	35.5
16-May-01	203	86	1188	264.0	37.0	19-May-01	206	92	1208	268.4	21.5
18-May-01	205	99	1142	253.8	2.5	20-May-01	207	94	1212	269.3	16.2
19-May-01	206	99	1208	268.4	2.7	21-May-01	208	89	1121	249.1	27.4
20-May-01	207	96	1212	269.3	10.8	23-May-01	210	95	1288	286.2	14.3
21-May-01	208	91	1121	249.1	22.4	24-May-01	211	99	1281	284.7	2.8
22-May-01	209	82	1304	289.8	52.2	26-May-01	213	98	1052	233.8	4.7
24-May-01	211	94	1281	284.7	17.1	27-May-01	214	94	1077	239.3	14.4
26-May-01	213	95	1052	233.8	11.7	28-May-01	215	93	1052	233.8	16.4
28-May-01	215	98	1162	258.2	5.2	29-May-01	216	97	1217	270.4	8.1
30-May-01	217	92	1231	273.6	21.9	01-Jun-01	219	98	1205	267.8	5.4
31-May-01	218	96	1054	234.2	9.4	02-Jun-01	220	99	1161	258.0	2.6
01-Jun-01	219	96	1155	256.7	10.3	03-Jun-01	221	99	1135	252.2	2.5
02-Jun-01	220	98	1161	258.0	5.2	04-Jun-01	222	94	1168	259.6	15.6
05-Jun-01	223	97	1135	252.2	7.6	05-Jun-01	223	99	1135	252.2	2.5
06-Jun-01	224	96	1296	288.0	11.5	07-Jun-01	225	92	1204	267.6	21.4
07-Jun-01	225	93	1204	267.6	18.7	08-Jun-01	226	93	1125	250.0	17.5
08-Jun-01	226	94	1125	250.0	15.0	09-Jun-01	227	95	1225	272.2	13.6
10-Jun-01	228	92	1210	268.9	21.5	11-Jun-01	229	99	1225	272.2	2.7
11-Jun-01	229	98	1225	272.2	5.4	13-Jun-01	231	94	1194	265.3	15.9
12-Jun-01	230	99	1127	250.4	2.5	14-Jun-01	232	96	1112	247.1	9.9
14-Jun-01	232	95	1112	247.1	12.4	17-Jun-01	235	99	1167	259.3	2.6
16-Jun-01	234	96	1200	266.7	10.7						
17-Jun-01	235	93	1167	259.3	18.2						
20-Jun-01	238	92	1157	257.1	20.6						
Average		94.9	1189	264.2	13.6	Average		94.2	1188	264.0	15.2

Table A2 – 28

MBR Operating Incidents

Date	Day	Reactor	Problem
Nov. 1, 2001	7	R1	Excess foam was observed and caused loss of mixed liquor.
Nov. 6, 2001	12	R2	Excess foam was observed and caused loss of mixed liquor.
Dec. 8, 2001	44	R1	The bearing of the recirculation pump wore out and failed to pump the mixed liquor through membrane unit. Therefore, the mixed liquor overflowed. A volume of 1 litre of mixed liquor was lost.
Dec. 29, 2001	65	R2	The pH probe was damaged by leakage. It resulted in pumping remaining sodium hydroxide solution into the reactor. The pH increased to 9.2. Therefore, the mixed liquor was partly replaced by the mixed liquor from the backup reactor. The containers of sodium hydroxide were replaced by smaller bottle to minimize the damage if it happened again.
Jan. 23, 2001	90	R2	The permeate solenoid valve was malfunctioned by overheat. The mixed liquor level in the reactor increases to the lid of the reactor, causing splashing and the loss of some mixed liquor.
Feb. 16, 2001	114	R1	A programming error in the control timer caused the overload of evaporator condensate. It resulted in decreased removal efficiencies.
Mar. 1, 2001	127	R2	The connection between the temperature probe and temperature controller was not tight enough and resulted in wrong temperature signal. The system was cooled to 53 °C and gradually heated back to 60 °C after the problem was fixed.
Mar. 14, 2001	140	R2	The pH probe was damaged by leakage. It resulted in pumping remaining sodium hydroxide solution into the reactor. The pH increased to 8.3. Therefore, the mixed liquor was partly replaced by the mixed liquor from the backup reactor. The pH probe for R1 was replaced by another model, but the port for pH probe of R2 was too small for the replacement.
Apr. 17, 2001	174	R1	Excess foam was observed and caused loss of mixed liquor.
May 2, 2001	189	R1	Feed valve was clogged by solids and resulted in no feed into R1 for 12 hrs.

Appendix 3 Data Collected During Methanol Shock Loading Experiment

Appendix 3 contains the data collected during methanol shock loading experiment. Results from first, second, and third shock loading tests monitoring removal kinetics of methanol and total organic carbon (TOC) are presented in Table A3 – 1 to A3 – 5, Table A3 – 6 to A3 – 10, and Table A3 – 11 to A3 - 15. Some batch tests were performed during the methanol shock loading tests and are summarized in Table A3 – 16 to A3 – 21. For these tables, the parameter K is the zero order coefficient for the biological removal of contaminant (mg/L·min). The parameter Co is the initial concentration in the MBR and the parameter Ce is the final TOC concentration in the MBR, derived from the second zero order removal coefficient. The R^2 value is the coefficient of determination for linear regression.

The calculations for observed growth yields of R1 and R2 are presented in Table A3 – 22 and Table A3 - 23.

Results of colour tests during methanol shock loading tests are summarized in Table A3 - 24.

Methanol Shock Loading Test 1 - June 25, 2001 (1800 mg / L)

Table A3 - 1 Batch Cycle 1

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	320.7	188	349.8	186
30	276.6	167	307.7	157
45	197.1	131	249.9	129
60	133.9	112	199.5	110
75	56.8	95	157.4	93
90	0	87	101.7	84
Co (Ce)	398.2	215.5 (60.9)	401.9	209.5 (56.3)
K	4.5	1.76 0.83	3.3	1.71 0.87
R²	0.993	0.985 0.959	0.998	0.992 0.969

Table A3 - 5 Batch Cycle 5

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	200.6	131	214.5	123
30	135.9	107	158.8	97
45	71.5	96	106.5	80
60	8.2	73	51.7	62
75	0	66	0.0	53
90	0	58	0	49
Co (Ce)	264.8	148 (43.2)	268.2	140.5 (35.6)
K	4.3	1.23 0.5	3.6	1.33 0.43
R²	0.979	0.982 0.999	0.989	0.99 0.953

Table A3 - 2 Batch Cycle 2

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
30	281.4	144.2	174.3	109
60	201.4	93.6	80.3	77
90	56.4	77.9	0	49
Co (Ce)	404.8	171.5 (64.2)	259.2	138.3 (33.1)
K	3.8	1.1	2.9	1.0
R²	0.973	0.915	0.998	0.999

Table A3 - 3 Batch Cycle 3

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
30	290.6	133	190.7	93
60	173.9	97	52.9	65
90	66.5	63	3.3	39
Co (Ce)	401.1	165.7 (60.4)	269.7	119.3 (32.3)
K	3.7	1.1	3.1	0.9
R²	0.999	0.989	0.931	0.991

Table A3 - 4 Batch Cycle 4

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
30	281.4	123	201.6	99
60	180.9	89	51.1	64
90	71.4	60	7.4	38
Co (Ce)	387.9	153.7 (59.8)	280.9	128 (30.9)
K	3.5	1.1	3.2	1.0
R²	0.999	0.998	0.908	0.993

Methanol Shock Loading Test 2 - June 28, 2001 (2400 mg / L)

Table A3 - 6 Batch Cycle 1

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	451.7	216	468.2	224
30	366.1	175	410.2	187
45	282.4	146	349.4	145
60	196.9	104	285.9	110
75	114.3	86	226.3	86
90	31.1	77	164.3	81
Co (Ce)	533.8	251.5 (48.5)	532.8	262.5 (48.4)
<i>K</i>	5.6	2.43 0.9	4.1	2.56 0.97
<i>R</i> ²	0.978	0.995 0.964	0.984	0.999 0.875

Table A3 - 10 Batch Cycle 5

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	214.3	136	215.6	140
30	157.8	114	164.8	114
45	103.1	96	111.7	102
60	45.9	72	61.8	78
75	0	64	11	71
90	0	59	0	66
Co (Ce)	268.7	157 (45.9)	266.4	158 (53.7)
<i>K</i>	3.7	1.4 0.43	3.4	1.32 0.4
<i>R</i> ²	0.942	0.997 0.983	0.966	0.983 0.991

Table A3 - 7 Batch Cycle 2

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	446.4	183	199.6	85
45	265.2	132	61.2	53
75	88.7	77	0	31
Co (Ce)	536.4	207.5 (55.6)	268.2	95.2 (33.8)
<i>K</i>	6.0	1.7	4.6	0.9
<i>R</i> ²	0.9821	0.864	0.995	0.995

Table A3 - 8 Batch Cycle 3

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	470.7	240	181.7	95
45	316.8	189	74.6	66
75	200.9	131	0	37
Co (Ce)	531.8	268.8 (62.1)	264.8	106 (29.4)
<i>K</i>	4.5	1.8	3.6	0.9
<i>R</i> ²	0.993	0.999	0.999	0.946

Table A3 - 9 Batch Cycle 4

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	465.9	224	186.5	91
45	334.8	188	82.9	60
75	254.3	157	0	33
Co (Ce)	510.4	239.9 (107.9)	238.3	106 (31.7)
<i>K</i>	3.5	1.1	3.5	1
<i>R</i> ²	0.981	0.998	0.999	0.946

Methanol Shock Loading Test 2 - July 2, 2001 (3000 mg / L)

Table A3 - 11 Batch Cycle 1

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	643.1	265	647.2	238
30	624.3	262	625.8	234
45	601.9	254	604.3	231
60	574.3	248	579.6	224
75	554.6	243	558.1	220
90	533.1	238	536.6	214
Co (Ce)	668.4	273.2	670.6	243.3
<i>K</i>	1.5	0.4	1.5	0.3
<i>R</i> ²	0.966	0.954	0.882	0.984

Table A3 - 15 Batch Cycle 5

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	1512.6	612	615.2	184
30	1466.5	604	546.3	174
45	1418.7	596	536.7	170
60	1363.2	572	502.6	164
75	1330.5	556	428.9	152
90	1274.8	528	427	146
Co (Ce)	1559.6	636.8	642.2	191.2
<i>K</i>	3.1	1.1	2.5	0.5
<i>R</i> ²	0.997	0.954	0.946	0.983

Table A3 - 12 Batch Cycle 2

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	1090.4	400	725.9	264
45	1005.9	384	651.3	256
75	927.5	371	598.8	250
Co (Ce)	1129.9	408	754	267.2
<i>K</i>	2.7	0.5	2.1	0.2
<i>R</i> ²	0.98	0.999	0.99	0.993

Table A3 - 13 Batch Cycle 3

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	1314.4	537	676.6	252
45	1230.6	529	624.5	238
75	1149.9	523	561.1	220
Co (Ce)	1352.9	540.2	707.4	259
<i>K</i>	2.7	0.2	1.9	0.5
<i>R</i> ²	0.999	0.993	0.997	0.999

Table A3 - 14 Batch Cycle 4

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	1634.5	687	649.8	252
45	1534.7	665	588.6	238
75	1465.3	651	516.7	220
Co (Ce)	1671.7	694.7	684.9	259
<i>K</i>	2.9	0.6	2.2	0.5
<i>R</i> ²	0.989	0.984	0.998	0.999

Contaminant Removal Data During the Test Period of Methanol Shock Loading Tests

Table A3 - 16 Batch Test on June 26, 2001

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	194.9	139	230.5	139
30	143.4	118	188.2	114
45	92.6	103	151.3	107
60	44.7	86	105.6	76
75	2.8	78	74.2	66
90	0	72	33.9	61
Co (Ce)	240.5	155	267.7	158
K	3.2	1.16	2.6	1.31
R ²	0.998	0.995	0.998	0.952
				0.964

Table A3 - 19 Batch Test on July 3, 2001

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	509.1	274	226.4	140
30	458.3	256	190.7	125
45	384.1	236	163.7	103
60	361.4	229	131.5	85
75	309.8	221	105.2	79
90	254.3	213	75.1	72
Co (Ce)	553.7	279.9	253.3	160
K	3.3	0.79	2	1.25
R ²	0.988	0.949	0.998	0.995
				0.998

Table A3 - 17 Batch Test on June 29, 2001

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	237.6	152	244.4	143
30	176.6	135	202.7	124
45	108.1	114	166.5	102
60	60.2	96	118.3	79
75	3.0	86	76.4	71
90	0	75	36.3	65
Co (Ce)	292.8	171.5	287.5	165.5
K	3.9	1.26	2.8	1.43
R ²	0.997	0.999	0.999	0.998
				0.993

Table A3 - 20 Batch Test on July 4, 2001

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	203.2	136	230.9	136
30	154.1	116	199.7	113
45	72.2	93	159.8	98
60	44.7	78	127.5	79
75	0	69	92.7	69
90	0	63	60.3	64
Co (Ce)	257.9	155	265.8	153
K	3.7	1.31	2.3	1.24
R ²	0.969	0.994	0.999	0.994
				0.964

Table A3 - 18 Batch Test on July 1, 2001

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	237.4	149	225.9	154
30	181.1	136	175.7	129
45	124.5	112	132.3	113
60	54.2	96	82.8	89
75	39.3	82	39.3	81
90	0	77	0	76
Co (Ce)	284.2	169	271	174
K	3.5	1.22	3.1	1.41
R ²	0.974	0.988	0.999	0.993
				0.983

Table A3 - 21 Batch Test on July 5, 2001

Time (min)	Reactor 1		Reactor 2	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	203.9	144	240.9	157
30	155.4	124	200.3	131
45	101.2	96	171.4	118
60	40.3	80	125.8	86
75	0	76	84.6	81
90	0	69	55.7	73
Co (Ce)	261.5	166	278.3	179.5
K	3.6	1.47	2.5	1.51
R ²	0.997	0.99	0.997	0.977
				0.983

Table A3 - 22 Growth Yield of Reactor 1 During Period of Methanol Shock loading Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
23-Jun-01	0	458	2867	140	0	0
24-Jun-01	1	447	3033	149	5364	149
25-Jun-01-Cycle1	2	716	3033	149	11444	297
25-Jun-01-Cycle2		702	3033	149	12146	
25-Jun-01-Cycle3		708	3033	149	12854	
25-Jun-01-Cycle4		696	3033	149	13550	
25-Jun-01-Cycle5		478	3033	149	14028	
26-Jun-01	3	482	3333	163	17402	787
27-Jun-01	4	458	3333	163	22898	951
28-Jun-01-Cycle 1	5	948	3333	163	29342	1114
28-Jun-01-Cycle 2		954	3333	163	30296	
28-Jun-01-Cycle 3		942	3333	163	31238	
28-Jun-01-Cycle 4		938	3333	163	32176	
28-Jun-01-Cycle 5		488	3333	163	32664	
29-Jun-01	6	496	3500	172	36136	2143
30-Jun-01	7	433	3500	172	41332	2314
1-Jul-01	8	487	3567	175	47176	2489
2-Jul-01-Cycle 1	9	336	2833	139	53356	2628
2-Jul-01-Cycle 2		602	2833	139	53958	
2-Jul-01-Cycle 3		616	2833	139	54574	
2-Jul-01-Cycle 4		647	2833	139	55221	
2-Jul-01-Cycle 5		702	2833	139	55923	
3-Jul-01	10	318	2833	139	58149	2767
4-Jul-01	11	386	2967	145	62781	2912
5-Jul-01	12	405	2967	145	67641	3058
6-Jul-01	13	454	3267	160	73089	3218
7-Jul-01	14	448	3267	160	78465	3378
8-Jul-01	15	439	3267	160	83733	3538
9-Jul-01	16	452	3267	160	89157	3698
					Growth Yield	0.0415

*Measured MLVSS Value in Bold.

Table A3 - 23 Growth Yield of Reactor 2 During Period of Methanol Shock loading Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
23-Jun-01	0	468	3067	159	0	0
24-Jun-01	1	436	3267	170	5616	170
25-Jun-01-Cycle1	2	732	3267	170	11580	340
25-Jun-01-Cycle2		478	3267	170	12058	
25-Jun-01-Cycle3		505	3267	170	12563	
25-Jun-01-Cycle4		492	3267	170	13055	
25-Jun-01-Cycle5		498	3267	170	13553	
26-Jun-01	3	487	3403	177	16962	517
27-Jun-01	4	479	3403	177	22710	694
28-Jun-01-Cycle 1	5	937	3403	177	29395	871
28-Jun-01-Cycle 2		505	3403	177	29900	
28-Jun-01-Cycle 3		496	3403	177	30396	
28-Jun-01-Cycle 4		492	3403	177	30888	
28-Jun-01-Cycle 5		498	3403	177	31386	
29-Jun-01	6	483	3533	184	34767	1054
30-Jun-01	7	477	3650	190	40491	1244
1-Jul-01	8	469	3650	190	46119	1434
2-Jul-01-Cycle 1	9	332	3700	192	52079	1626
2-Jul-01-Cycle 2		468	3700	192	52547	
2-Jul-01-Cycle 3		362	3700	192	52909	
2-Jul-01-Cycle 4		377	3700	192	53286	
2-Jul-01-Cycle 5		560	3700	192	53846	
3-Jul-01	10	442	3700	192	56940	1819
4-Jul-01	11	453	3833	199	62376	2018
5-Jul-01	12	467	3833	199	67980	2217
9-Jul-01	16	472	3900	203	90636	3029
Growth Yield						0.0334

*Measured MLVSS Value in Bold.

Table A3 - 24 Colour Data of Reactor 2 During Period of Methanol Shock loading Tests

	<i>Reactor 1</i>				<i>Reactor 2</i>			
	Condensate		Permeate		Condensate		Permeate	
	Apparent	True	True	pH	Apparent	True	True	pH
17-Jun-01	700	400	200	7.44	700	400	200	7.12
18-Jun-01	700	400	160	6.54	700	400	210	7.4
19-Jun-01	700	420	210	6.66	700	420	160	6.93
21-Jun-01	720	420	240	6.93	720	420	200	7.17
22-Jun-01	750	450	200	7.66	750	450	160	7.31
25-Jun-01	750	450	200	7.02	750	450	160	7.25
26-Jun-01	700	400	160	6.78	700	400	160	6.78
27-Jun-01	800	500	160	7.5	800	500	200	7.5
28-Jun-01	700	400	160	7.72	700	400	160	7.07
29-Jun-01	700	420	210	8.07	700	420	200	7.45
30-Jun-01	680	400	210	7.3	680	400	210	7.66
1-Jul-01	750	420	210	7.23	750	420	200	7.6
2-Jul-02	700	400	280	7.37	700	400	240	7.35
3-Jul-01	700	400	280	7.17	700	400	260	7.12
4-Jul-01	700	420	210	7.04	700	420	240	6.86
5-Jul-01	720	420	240	7.17	720	420	220	7.17
6-Jul-01	750	450	240	7.13	750	450	260	7.11
7-Jul-01	750	450	220	7.15	750	450	240	6.52

Appendix 4 Data Collected During Black liquor Carryover Experiment

Appendix 4 contains the data collected during black liquor carryover experiment. Results from first, second, third, and fourth shock loading tests monitoring removal kinetics of methanol, total organic carbon (TOC) and chemical oxygen demand (COD) are presented in Table A4 – 1 to A4 – 5, Table A4 – 6 to A4 – 10, Table A4 – 11 to A4 – 15, and Table A4 – 16 to A4 - 20. Some batch tests were performed during the black liquor carryover tests and are summarized in Table A4 – 21 to A4 – 29. For these tables, the parameter K is the zero order coefficient for the biological removal of contaminant (mg/L-min). The parameter C_0 is the initial concentration in the MBR and the parameter C_e is the final TOC concentration in the MBR, derived from the second zero order removal coefficient. The R^2 value is the coefficient of determination for linear regression.

The calculations for observed growth yields of R1 and R2 are presented in Table A4 – 30 to table A4 - 33.

Results of colour tests during black liquor carryover tests are summarized in Table A4 - 34.

Results of solid tests during black liquor carryover tests are summarized in Table A4 - 35.

Black Liquor CarryOver (BL) Test 1 - August 4, 2001 (4 mL BL/ L Condensate)

Table A4 - 1 Contaminant Removal of BL Test 1 - Batch Cycle 1

Time (min)	Reactor 1				Reactor 2			
	Methanol (mg/L)	TOC (mg/L)		COD (mg/L)	Methanol (mg/L)	TOC (mg/L)		COD (mg/L)
15	216.2	165		664	220.8	160		679
30	187.8	142		654	193.5	141		613
45	169	133		597	165.8	124		524
60	128.5	109		568	132.1	101		486
75	103.4	101		549	82.6	95		430
90	72.4	94		473	59.2	87		357
Co (Ce)	247.5	181.5	78.8	714.7	259.8	180	72.9	734.5
<i>K</i>	1.9	1.18	0.5	2.5	2.2	1.29	0.47	4.2
R ²	0.994	0.974	0.999	0.954	0.99	0.996	0.993	0.991

Table A4 - 2 Contaminant Removal of BL Test 1 - Batch Cycle 2

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
30	192.7	160	670	178.6	170	587
60	149.7	128	633	125.4	146	450
90	77.1	102	554	40.2	129	333
Co (Ce)	255.4	188	735	253.1	189.3	710.7
<i>K</i>	2	1	1.9	2.3	0.7	4.2
<i>R</i> ²	0.979	0.996	0.958	0.983	0.99	0.998

Table A4 - 3 Contaminant Removal of BL Test 1 - Batch Cycle 3

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
30	196.8	155	716	183.2	165	566
60	132.5	126	643	107.4	140	473
90	83.6	93	582	65.5	129	388
Co (Ce)	250.8	186.7	781	236.4	180.7	653.7
<i>K</i>	1.9	1	2.2	2	0.6	3
<i>R</i> ²	0.994	0.999	0.997	0.973	0.952	0.999

Black Liquor CarryOver (BL) Test - August 4, 2001 (4 mL BL/ L Condensate) - Con't

Table A4 - 4 Contaminant Removal of BL Test 1 - Batch Cycle 4

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
30	185.7	166	720	158.3	158	528
60	155.6	129	606	52.2	132	400
90	79.8	112	501	2.5	115	332
Co (Ce)	246.3	189.7	828	226.8	178	616
<i>K</i>	1.8	0.9	3.7	2.6	0.7	3.3
<i>R</i> ²	0.942	0.956	0.999	0.958	0.986	0.97

Table A4 - 5 Contaminant Removal of BL Test 1 - Batch Cycle 5

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	212.6	158	851	210.2	158	592
30	198.2	139	803	188.4	146	544
45	168.8	110	779	143.2	131	528
60	134.5	102	739	116.5	109	498
75	86.3	92	713	98.8	101	480
90	64.1	87	679	65.4	92	444
Co (Ce)	255.4	176.5	71.2	239	176.5	74.8
<i>K</i>	2.1	1.31	0.5	2.2	1.9	1.08
<i>R</i> ²	0.971	0.961	0.964	0.993	0.987	0.981

Black Liquor CarryOver (BL) Test 2 - August 7, 2001 (8 mL BL/ L Condensate)

Table A4 - 6 Contaminant Removal of BL Test 2 - Batch Cycle 1

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	208.4	219	722	218.9	221	772
30	170.7	193	633	181.3	203	732
45	160.2	178	613	158.8	179	673
60	123.6	159	563	126.8	156	653
75	86.2	146	424	96.5	148	633
90	42.7	142		64.8	141	
Co (Ce)	243.8	236	123.1	246.9	244.5	125.83
<i>K</i>	2.1	1.3	0.57	2	1.46	0.5
<i>R</i> ²	0.978	0.988	0.915	0.998	0.996	0.999

Table A4 - 7 Contaminant Removal of BL Test 2 - Batch Cycle 2

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	208.7	204	737	218.6	210	1001
45	131.4	173	680	158.7	189	927
75	68.8	155	535	85.1	174	837
Co (Ce)	241.2	214.1	802.2	254.3	218	1044.7
<i>K</i>	2.3	0.8	3.4	2.2	0.6	2.7
<i>R</i> ²	0.996	0.977	0.941	0.997	0.991	0.997

Table A4 - 8 Contaminant Removal of BL Test 2 - Batch Cycle 3

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	182.1	210	753	211.5	202	1011
45	128.1	185	659	139.7	175	910
75	31.3	168	536	86.4	135	799
Co (Ce)	226.9	219.2	812.1	239.7	220.9	1065.7
<i>K</i>	2.5	0.7	3.6	2.1	1.1	3.5
<i>R</i> ²	0.974	0.988	0.994	0.993	0.988	0.999

Black Liquor CarryOver (BL) Test - August 7, 2001 (8 mL BL/ L Condensate) - Con't

Table A4 - 9 Contaminant Removal of BL Test 2 - Batch Cycle 4

Time (min)	<i>Reactor 1</i>			<i>Reactor 2</i>		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	206.9	200	733	196.8	195	923
45	154.3	177	653	115.8	166	836
75	61.9	160	534	82.5	143	712
Co (Ce)	249.8	209	789.3	217.4	207	981.9
<i>K</i>	2.4	0.7	3.3	1.9	0.9	3.5
<i>R</i> ²	0.976	0.993	0.987	0.945	0.996	0.99

Table A4 - 10 Contaminant Removal of BL Test 2 - Batch Cycle 5

Time (min)	<i>Reactor 1</i>			<i>Reactor 2</i>			
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	
15	205.4	202	713	202.3	210	824	
30	188.6	195	683	174.3	195	755	
45	170.3	181	629	155.5	182	695	
60	121.8	158	594	123.1	161	631	
75	96.3	148	534	89.5	157	573	
90	72.4	143		68.4	148		
Co (Ce)	241.5	220.5	127.2	764.7	231.2	227	136.2
<i>K</i>	1.9	0.97	0.5	3	1.8	1.07	0.43
<i>R</i> ²	0.978	0.943	0.964	0.989	0.994	0.989	0.953
							0.999

Black Liquor CarryOver (BL) Test -3 August 10, 2001 (12 mL BL/ L Condensate)

Table A4 - 11 Contaminant Removal of BL Test 3 - Batch Cycle 1

Time (min)	Reactor 1			Reactor 2				
	Methanol (mg/L)	TOC (mg/L)		COD (mg/L)	Methanol (mg/L)	TOC (mg/L)		COD (mg/L)
15	232.3	223		673	215.9	237		683
30	190.2	200		624	167.8	209		653
45	140.4	185		554	138.7	195		614
60	57.6	166		524	91	176		495
75	43.1	160		465	63.8	166		475
90	20.2	147			17.6	160		376
Co (Ce)	272.4	240	129.6	722.8	250.9	253.5	143.7	768.1
K	3	1.24	0.63	3.4	2.6	1.31	0.53	4.2
R ²	0.956	0.994	0.957	0.99	0.995	0.981	0.98	0.959

Table A4 - 12 Contaminant Removal of BL Test 3 - Batch Cycle 2

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	230.2	236	663	207	240	771
45	164.2	210	586	115.8	215	654
75	87.5	192	478	32.1	181	512
Co (Ce)	267.7	245.7	714.4	249.5	256.3	839.9
K	2.4	0.7	3.1	2.9	1	4.3
R ²	0.998	0.989	0.991	0.991	0.992	0.997

Table A4 - 13 Contaminant Removal of BL Test 3 - Batch Cycle 3

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	230.9	259	788	214.3	265	798
45	162.9	232	723	118.3	231	668
75	104.9	216	620	54.8	203	589
Co (Ce)	260.7	267.9	836.3	248.8	279.5	841.8
K	2.1	0.7	2.8	2.7	1	3.5
R ²	0.998	0.979	0.983	0.987	0.997	0.981

Black Liquor CarryOver (BL) Test - August 10, 2001 (12 mL BL/ L Condensate) - Con't

Table A4 - 14 Contaminant Removal of BL Test 3 - Batch Cycle 4

Time (min)	<i>Reactor 1</i>			<i>Reactor 2</i>		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	215.4	266	816	229.2	289	771
45	133.8	235	721	143.2	254	676
75	74.3	219	578	83.1	231	513
Co (Ce)	247.0	275.3	883.5	261.4	301.5	846.8
<i>K</i>	2.4	0.8	4	2.4	1	4.3
<i>R</i> ²	0.992	0.967	0.987	0.99	0.986	0.978

Table A4 - 15 Contaminant Removal of BL Test 3 - Batch Cycle 5

Time (min)	<i>Reactor 1</i>			<i>Reactor 2</i>		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	223.3	297	890	220.1	322	938
30	199.7	280	827	168.8	294	854
45	149.8	245	782	123.4	276	788
60	120.4	227	713	75.4	259	716
75	98.7	210	637	36.8	244	638
90	54.6	206		0	240	
Co (Ce)	258.7	323.5	182.8	262.9	343.3	219.2
<i>K</i>	2.2	1.63	0.7	3.1	1.53	0.63
<i>R</i> ²	0.989	0.98	0.887	0.993	0.998	0.985

Black Liquor CarryOver (BL) Test 4 - August 16, 2001 (24 mL BL/ L Condensate)

Table A4 - 16 Contaminant Removal of BL Test 4 - Batch Cycle 1

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	231.8	324	870	238.5	326	904
30	212.6	308	798	196.9	302	858
45	177.3	296	756	158.7	280	744
60	142.2	287	723	133.9	259	715
75	118.7	273	648	104.5	238	673
90	95.6	261	588	58.7	223	610
Co (Ce)	262.8	334.4	919.8	268.6	344.1	956.1
<i>K</i>	1.9	0.8	3.6	2.3	1.4	3.9
<i>R</i> ²	0.992	0.995	0.988	0.993	0.996	0.97

Table A4 - 17 Contaminant Removal of BL Test 4 - Batch Cycle 2

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	276.5	478	997	265.9	287	876
45	247.6	432	887	216.7	258	772
75	194.5	411	805	144.3	238	649
Co (Ce)	301.0	490.6	1040.3	300.2	297.8	935.9
<i>K</i>	1.4	1.1	3.2	2	0.8	3.8
<i>R</i> ²	0.972	0.956	0.993	0.988	0.989	0.998

Table A4 - 18 Contaminant Removal of BL Test 4 - Batch Cycle 3

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	332.3	594	1131	267.6	281	866
45	271.2	567	1029	208.8	260	745
75	247.1	525	958	135.5	226	635
Co (Ce)	347.4	613.8	1169.1	303	296.9	921.9
<i>K</i>	1.4	1.2	2.9	2.2	0.9	3.9
<i>R</i> ²	0.941	0.985	0.99	0.996	0.982	0.999

Black Liquor CarryOver (BL) Test - August 16, 2001 (24 mL BL/ L Condensate) - Con't

Table A4 - 19 Contaminant Removal of BL Test 4 - Batch Cycle 4

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	417.8	696	1285	235.6	275	824
45	376.5	668	1189	195.7	257	720
75	351.8	636	1138	112.6	242	596
Co (Ce)	431.5	711.7	1314.3	273.6	282.8	884.3
K	1.1	1	2.5	2.1	0.6	3.8
R²	0.979	0.999	0.97	0.961	0.997	0.997

Table A4 - 20 Contaminant Removal of BL Test 4 - Batch Cycle 5

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	529.8	687	1547	232.7	262	745
30	527.5	675	1487	187.6	244	697
45	525.1	660	1487	143.9	239	645
60	494.4	642	1428	125.8	219	578
75	475	629	1378	80.2	211	488
90	413.7	614	1368	50.3	205	433
Co (Ce)	571.1	703.3	1577.3	262	270.4	823.1
K	1.5	1	2.4	2.4	0.8	4.3
R²	0.83	0.998	0.956	0.99	0.968	0.99

Contaminant Removal Data During the Test Period of Black Liquor CarryOver Tests

Table A4 - 21 Batch Test on August 3, 2001

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	187.5	139	214.9	149
30	141.8	118	163.4	128
45	87.8	93	96.2	103
60	28.6	82	60.7	88
75	0	75	18.2	79
90	0	69	0	74
Co (Ce)	244.1	157	259.5	169
K	3.5	1.3	3.3	1.39
R ²	0.997	0.98	0.988	0.99

Table A4 - 24 Batch Test on August 11, 2001

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	254.6	157	234.5	156
30	198.7	129	198.6	136
45	143.2	97	164.5	114
60	98.8	88	123.4	87
75	53.2	80	66.7	79
90	0	73	24.5	75
Co (Ce)	300.5	178	284.1	181
K	3.4	1.6	2.8	1.53
R ²	0.997	0.96	0.992	1

Table A4 - 22 Batch Test on August 5, 2001

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	234.4	152	231.5	170
30	173.6	138	196.6	152
45	105.5	109	138.7	139
60	54.6	84	90.2	113
75	0	79	54.4	103
90	0	71	11.3	95
Co (Ce)	293.9	179	278.1	190
K	4.1	1.55	3.0	1.23
R ²	0.997	0.98	0.995	0.98

Table A4 - 25 Batch Test on August 13, 2001

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	213.8	136	205	136
30	176.9	116	165.2	117
45	100.5	93	92.4	93
60	64.3	74	63.7	74
75	19.8	69	18.4	69
90	0	62	0	65
Co (Ce)	265.2	157	251.4	158
K	3.3	1.39	3.2	1.4
R ²	0.985	1	0.984	1

Table A4 - 23 Batch Test on August 8, 2001

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	237.4	147	227.6	143
30	174.3	124	193.5	115
45	114.7	101	144.8	92
60	46.8	81	102.5	79
75	15.8	75	74.5	71
90	0	68	15.8	65
Co (Ce)	289	169	272.3	161
K	3.8	1.47	2.8	1.43
R ²	0.988	1	0.994	0.98

Table A4 - 26 Batch Test on August 15, 2001

Time (min)	<i>Reactor 1</i>		<i>Reactor 2</i>	
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)
15	209.9	144	207.8	134
30	169.8	124	165.6	119
45	121.5	96	121.1	98
60	71.7	80	86.7	75
75	26.4	74	44.8	70
90	0	69	0	64
Co (Ce)	259.4	166	246.7	156
K	3.1	1.47	2.7	1.32
R ²	0.999	0.99	0.999	0.99

Contaminant Removal Data During the Test Period of Black Liquor CarryOver Tests - Con't

Table A4 - 27 Batch Test on August 17, 2001

Time (min)	Reactor 1		Reactor 2		
	Methanol (mg/L)	TOC (mg/L)	Methanol (mg/L)	TOC (mg/L)	
15	476.6	243	223.3	136	
30	438.3	228	185.2	121	
45	401.9	213	150	104	
60	372.2	198	105.5	86	
75	355.4	184	77.4	76	
90	336.8	166	26.8	70	
Co (Ce)	494.6	258.2	263.1	154	53.7
K	1.9	1.01	2.6	1.11	0.53
R ²	0.972	0.999	0.996	1	0.98

Table A4 - 28 Batch Test on August 18, 2001

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)		Methanol (mg/L)	TOC (mg/L)	
15	222.2	126		213.2	126	
30	175.4	107		154.1	107	
45	123.8	84		97.8	83	
60	96.5	67		64.5	68	
75	64.3	60		46.5	62	
90	19.7	54		0	57	
Co (Ce)	254.3	146	41.2	242.1	146	45.4
K	2.6	1.33	0.43	2.8	1.32	0.37
R ²	0.991	1	1	0.956	0.99	1

Table A4 - 29 Batch Test on August 19, 2001

Time (min)	Reactor 1			Reactor 2		
	Methanol (mg/L)	TOC (mg/L)		Methanol (mg/L)	TOC (mg/L)	
15	213.3	131		203.2	129	
30	168.8	111		168.8	108	
45	94.5	85		110.5	87	
60	67.1	69		71.8	69	
75	33.8	63		23.5	61	
90	0	55		0	58	
Co (Ce)	253.7	152	40.9	252.5	149	45.8
K	3.1	1.41	0.47	3	1.34	0.37
R ²	0.971	0.99	0.99	0.995	1	0.94

Table A4 - 30 Growth Yield of Reactor 1 During Acclimatization before Black Liquor CarryOver Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
16-Jul-01	0	432	2150	105	0	0
19-Jul-01	3	477	2683	131	17172	394
25-Jul-01	9	458	2900	142	50148	1247
27-Jul-01	11	462	2683	131	61236	1510
30-Jul-01	14	449	2667	131	77400	1902
1-Aug-01	16	473	2767	136	88752	2173
Growth Yield						0.0245

Table A4 - 31 Growth Yield of Reactor 1 During Period of Black Liquor CarryOver Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
3-Aug-01	0	441	2533	133	0	0
4-Aug-01-Cycle 1	1	392	2533	124	392	0
4-Aug-01-Cycle 2		432	2533	124	824	
4-Aug-01-Cycle 3		414	2533	124	1238	
4-Aug-01-Cycle 4		393	2533	124	1631	
4-Aug-01-Cycle 5		302	2533	124	1933	
5-Aug-01	2	421	2533	124	4880	133
7-Aug-01-Cycle 1	4	449	2307	113	15656	359
7-Aug-01-Cycle 2		432	2307	113	16088	
7-Aug-01-Cycle 3		403	2307	113	16491	
7-Aug-01-Cycle 4		440	2307	113	16931	
7-Aug-01-Cycle 5		426	2307	113	17357	
8-Aug-01	5	448	2307	113	20493	472
10-Aug-01-Cycle 1	7	468	2307	113	32193	585
10-Aug-01-Cycle 2		482	2307	113	32675	
10-Aug-01-Cycle 3		453	2307	113	33128	
10-Aug-01-Cycle 4		448	2307	113	33576	
10-Aug-01-Cycle 5		468	2307	113	34044	
11-Aug-01	8	435	2307	113	37089	698
13-Aug-01	10	462	1833	90	48177	878
15-Aug-01	12	439	1833	90	58713	1057
16-Aug-01-Cycle 1	13	408	1833	90	41985	1147
16-Aug-01-Cycle 2		307	1833	90	42292	
16-Aug-01-Cycle 3		300	1833	90	42592	
16-Aug-01-Cycle 4		243	1833	90	42835	
16-Aug-01-Cycle 5		324	1833	90	43159	
17-Aug-01	14	338	1833	90	45525	1237
18-Aug-01	15	357	1900	93	49809	1330
20-Aug-01	17	410	1900	93	59649	1516
23-Aug-01	20	429	2017	99	75093	1813
Growth Yield						0.0241

*Measured MLVSS Value in Bold.

Table A4 - 32 Growth Yield of Reactor 2 During Acclimatization before Black Liquor CarryOver Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
16-Jul-01	0	448	2133	111	0	0
19-Jul-01	3	483	3000	156	17388	468
25-Jul-01	9	469	3217	167	51156	1472
27-Jul-01	11	475	2300	120	62556	1711
30-Jul-01	14	466	2433	127	79332	2090
1-Aug-01	16	482	2600	135	90900	2361
					Growth Yield	0.026

Table A4 - 33 Growth Yield of Reactor 2 During Period of Black Liquor CarryOver Tests

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
3-Aug-01	0	463	2617	136	0	0
4-Aug-01-Cycle 1	1	485	2617	136	485	136
4-Aug-01-Cycle 2		476	2617		961	
4-Aug-01-Cycle 3		442	2617		1403	
4-Aug-01-Cycle 4		430	2617		1833	
4-Aug-01-Cycle 5		445	2617		2278	
5-Aug-01	2	463	2617	136	5519	272
7-Aug-01-Cycle 1	4	462	2367	123	17093	518
7-Aug-01-Cycle 2		480	2367		17573	
7-Aug-01-Cycle 3		452	2367		18025	
7-Aug-01-Cycle 4		406	2367		18431	
7-Aug-01-Cycle 5		424	2367		18855	
8-Aug-01	5	448	2367	123	21991	641
10-Aug-01-Cycle 1	7	479	2367	123	33222	888
10-Aug-01-Cycle 2		477	2367		33699	
10-Aug-01-Cycle 3		473	2367		34172	
10-Aug-01-Cycle 4		515	2367		34687	
10-Aug-01-Cycle 5		460	2367		35147	
11-Aug-01	8	472	2367	123	38451	1011
13-Aug-01	10	460	2200	114	49491	1239
15-Aug-01	12	439	2200	114	60027	1468
16-Aug-01-Cycle 1	13	508	2200	114	66199	1583
16-Aug-01-Cycle 2		558	2200		66757	
16-Aug-01-Cycle 3		567	2200		67324	
16-Aug-01-Cycle 4		511	2200		67835	
16-Aug-01-Cycle 5		493	2200		68328	
17-Aug-01	14	475	2200	114	71653	1697
20-Aug-01	17	481	2817	146	88969	2137
					Growth Yield	0.024

*Measured MLVSS Value in Bold.

Table A4 - 34 Colour Data During Period of Black Liquor CarryOver Tests

	Reactor 1				Reactor 2			
	Condensate		Permeate		Condensate		Permeate	
	Apparent	True	True	pH	Apparent	True	True	pH
August 2	700	400	240	7.19	700	400	240	7.06
August 3	680	400	220	7.15	680	400	240	7.12
4-Aug-01 9:00	1000	800	240	7.23	1000	800	240	7.07
4-Aug-01 11:00	1000	800	240	7.15	700	400	240	7.07
4-Aug-01 13:00	1040	820	240	6.72	700	400	240	7.02
4-Aug-01 15:00	1040	820	220	6.96	700	400	220	7.1
4-Aug-01 17:00	700	400	240	7.01	700	400	240	6.97
August 5	700	420	240	7.41	700	420	240	6.96
August 6	720	420	310	6.71	720	420	310	6.84
7-Aug-01 9:00	1400	1000	240	7.01	1400	1000	240	6.97
7-Aug-01 11:00	700	400	210	6.8	1400	1000	240	6.75
7-Aug-01 13:00	700	400	240	7.22	1340	960	300	7.46
7-Aug-01 15:00	700	400	240	7.52	1400	100	420	6.09
7-Aug-01 17:00	700	400	240	7.13	700	400	420	7.27
August 9	700	380	360	7.04	700	380	240	6.54
10-Aug-01 9:00	1800	1200	280	6.6	1800	1200	240	6.46
10-Aug-01 11:00	660	350	240	6.38	1840	1200	240	6.33
10-Aug-01 13:00	660	350	240	7.39	1800	1180	350	6.81
10-Aug-01 15:00	660	350	240	6.48	1800	1200	310	6.63
10-Aug-01 17:00	660	350	240	6.37	660	350	310	6.61
August 11	750	450	350	6.73	750	450	310	6.75
August 12	750	450	240	6.99	750	450	300	6.69
August 13	700	400	240	6.96	700	400	300	6.72
August 14	800	500	350	6.57	800	500	490	6.45
August 15	700	400	280	6.57	700	400	310	6.36
16-Aug-01 9:00	2800	1400	280	6.87	2800	1400	240	6.4
16-Aug-01 11:00	2800	1400	350	7.05	700	420	280	6.62
16-Aug-01 13:00	2800	1400	420	7.14	700	420	310	6.77
16-Aug-01 15:00	2800	1400	560	6.77	700	420	310	6.7
16-Aug-01 17:00	700	420	600	7.28	700	420	350	6.46
August 17	680	400	680	5.98	680	400	510	6.69
August 18	750	420	490	6.89	750	420	490	6.53
August 20	660	360	350	7.79	660	360	300	6.59
August 21	700	400	280	6.5	700	400	250	6.74
August 22	700	400	350	7.63	700	400	280	6.64

Table A4 - 35 Solids Concentration Data During Period of Black Liquor CarryOver Tests

	Permeate from Reactor 1		Permeate from Reactor 2	
	TDS (mg/L)	VDS (mg/L)	TDS (mg/L)	VDS (mg/L)
August 2	1180	650	1520	970
August 3	1020	580	1500	760
4-Aug-01 9:00	1261	630	1550	517
4-Aug-01 11:00	1160	630	1260	580
4-Aug-01 13:00	1230	660	1420	700
4-Aug-01 15:00	1240	710	1480	780
4-Aug-01 17:00	1260	730	1450	760
August 5	800	350	1700	760
August 6	1440	930	1590	640
7-Aug-01 9:00	1440	710	1560	900
7-Aug-01 11:00	1610	890	1810	1040
7-Aug-01 13:00	1540	780	1940	1230
7-Aug-01 15:00	1190	440	1640	740
7-Aug-01 17:00	1340	520	1670	720
August 9	1605	590	1690	735
10-Aug-01 9:00	1420	630	2200	1260
10-Aug-01 11:00	1450	610	2190	1270
10-Aug-01 13:00	1430	620	2280	1280
10-Aug-01 15:00	1400	660	2340	1250
10-Aug-01 17:00	1560	770	2350	480
August 11	2360	640	1890	520
August 12	1680	520	1680	1240
August 13	2530	1400	1950	1570
August 14	2120	1400	1240	895
August 15	1420	585	1450	1020
16-Aug-01 9:00	1595	740	1660	980
16-Aug-01 11:00	1880	960	1620	1070
16-Aug-01 13:00	2000	990	1690	1300
16-Aug-01 15:00	2030	1060	1690	1350
16-Aug-01 17:00	3030	1610	2040	1480
August 17	2460	1530	1720	1250
August 18	1900	1340	1690	1100

Appendix 5 Data Collected During Mill Shutdown Experiment

Appendix 5 contains the data collected during mill shutdown experiment. Results from batch tests monitoring removal kinetics of methanol, total organic carbon (TOC), and chemical oxygen demand (COD) are presented in Table A5 – 1 to A5 – 9. For these tables, the parameter K is the zero order coefficient for the biological removal of contaminant (mg/L·min). The parameter Co is the initial concentration in the MBR and the parameter Ce is the final TOC concentration in the MBR, derived from the second zero order removal coefficient. The R^2 value is the coefficient of determination for linear regression.

The calculations for observed growth yields of R2 are presented in Table A5 –10.

Batch Test Data During Mill Shutdown Test

Table A5 - 1 August 25, 2001 (Day 2)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	259.7	202	838
30	243.9	199	809
45	237.7	197	760
60	225.5	196	730
75	203.1	191	662
90	198.3	183	642
Co (Ce)	272.2	206.7	885.3
<i>K</i>	0.8	0.2	2.8
<i>R</i> ²	0.974	0.897	0.984

Table A5 - 4 August 31, 2001 (Day 8)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	247.8	203	930
30	241.7	201	871
45	238.6	199	871
60	237.9	197	862
75	234.2	194	803
90	223.5	192	793
Co (Ce)	251.8	205.5	944.8
<i>K</i>	0.3	0.1	1.7
<i>R</i> ²	0.902	0.995	0.905

Table A5 - 2 August 27, 2001 (Day 4)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	314.3	219	850
30	300.6	209	762
45	289.9	208	713
60	281.7	204	703
75	272.6	202	683
90	261.4	199	595
Co (Ce)	322.4	219.3	869.9
<i>K</i>	0.7	0.2	2.9
<i>R</i> ²	0.994	0.904	0.92

Table A5 - 5 September 2, 2001 (Day 10)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	278.4	207	950
30	274.3	206	940
45	271.3	204	920
60	266.6	202	920
75	267.6	201	881
90	254.4	195	852
Co (Ce)	283.3	210.2	977.2
<i>K</i>	0.3	0.1	1.3
<i>R</i> ²	0.875	0.906	0.921

Table A5 - 3 August 29, 2001 (Day 6)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	286.1	210	846
30	282.4	204	846
45	280.4	203	806
60	270.3	202	738
75	264.9	200	689
90	260.2	199	679
Co (Ce)	293.5	209.8	904.7
<i>K</i>	0.4	0.1	2.6
<i>R</i> ²	0.968	0.869	0.941

Table A5 - 6 September 3, 2001 (Day 11)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	62.8	78	324
30	55.9	72	287
45	49.9	64	253
60	45.4	60	191
75	38.8	58	163
90	33.2	49	115
Co (Ce)	68.1	82.6	370.1
<i>K</i>	0.4	0.4	2.8
<i>R</i> ²	0.998	0.973	0.993

Table A5 - 7 September 4, 2001 (Day 12)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	111.1	137	496
30	96.7	133	443
45	81.3	124	404
60	60.2	113	337
75	49.5	108	315
90	28.3	99	274
Co (Ce)	128.9	146.6	534.3
K	1.1	0.5	3
R ²	0.995	0.988	0.986

Table A5 - 8 September 5, 2001 (Day 13)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	162	189	718
30	140.3	173	677
45	104.9	169	617
60	91.5	159	567
75	62.3	144	533
90	41.8	137	475
Co (Ce)	185.3	197.5	767.5
K	1.6	0.7	3.2
R ²	0.991	0.981	0.996

Table A5 - 9 September 6, 2001 (Day 14)

Time (min)	Reactor 1		
	Methanol (mg/L)	TOC (mg/L)	COD (mg/L)
15	210.8	223	813
30	185.5	215	727
45	151.4	188	678
60	117.6	184	613
75	83.5	164	587
90	56.9	158	499
Co (Ce)	245.2	236.9	858.3
K	2.1	0.9	3.9
R ²	0.998	0.964	0.983

Table A5 - 10 Growth Yield of Reactor 2 During Period of Mill Shutdown Test

Date	Cumulative Time (day)	Methanol Consumed (mg/cycle)	MLVSS (mg/L)	Sludge Wasted (mg/day)	Cumulative Methanol (mg)	Cumulative Solids (mg)
23-Aug-01	0	0	2383	124	0	0
24-Aug-01	1	0	2350	122	0	122
25-Aug-01	2	531	2350	122	531	244
26-Aug-01	3	0	2350	122	531	367
27-Aug-01	4	598	1617	84	1129	451
28-Aug-01	5	0	1617	84	1129	535
29-Aug-01	6	517	1350	70	1646	605
30-Aug-01	7	0	1350	70	1646	675
31-Aug-01	8	469	1250	65	2115	740
1-Sep-01	9	0	1250	65	2115	805
2-Sep-01	10	475	1300	68	2590	873
3-Sep-01	11	123	1300	68	2590	940
4-Sep-01	12	235	1383	72	4066	1012
5-Sep-01	13	346	1400	73	6886	1085
6-Sep-01	14	450	1683	88	11038	1173
Growth Yield						0.106

*Measured MLVSS Value in Bold.

Appendix 6 Data of Permeate Flux and Membrane Cleaning Procedure

Appendix 6 contains the data of permeate flux collected throughout entire experimental period. Results are presented in Table A6 – 1.

Based on discussions with Bérubé (2000) and supplier (US Filter), the membrane cleaning procedure was used during the present study and is presented as below.

Membrane Cleaning Procedure:

1. Disconnect the membrane unit with the flow restriction valve from the system
2. Drain the membrane unit and connect them to another progressive cavity pump
3. Close permeate ports (Figure 3.2) and open the valve so that the trans-membrane pressure is negligible.
4. Flush the system with water for 10 minutes
5. Rinse with a solution containing 200 to 300 ppm of NaOCl for 10 minutes
6. Pump clean water through membrane for 1 minute
7. Circulate a 20% NaOH solution through the membrane for 30 minutes
8. Pump a 20% NaOH solution through the membrane at trans-membrane pressure of 5-10 psi for 30 minutes.
9. Drain the membrane by opening both sides of permeate ports
10. Flush with distill water until pH of permeate is close to neutral (approximately 15 minutes)

11. Check permeate flow rate, which should be close to the rate that measure at the first clean water permeability test under the same condition, to confirm that the cleaning is complete

Table A6-1 Permeate Flux of Membrane During the Present Study

Reactor 1			Reactor 2			Reactor 1			Reactor 2		
Date	Day #	Flux (L/m ² h)	Date	Day #	Flux (L/m ² h)	Date	Day #	Flux (L/m ² h)	Date	Day #	Flux (L/m ² h)
26-Oct-00	1	160	26-Oct-00	1	150	22-May-01	209	100	28-May-01	215	60
29-Oct-00	4	130	28-Oct-00	3	130	24-May-01	211	90	29-May-01	216	50
31-Oct-00	6	100	31-Oct-00	6	110	26-May-01	213	90	01-Jun-01	219	40
04-Nov-00	10	90	05-Nov-00	11	90	28-May-01	215	80	02-Jun-01	220	80
07-Nov-00	13	80	07-Nov-00	13	80	30-May-01	217	90	03-Jun-01	221	70
10-Nov-00	16	70	09-Nov-00	15	80	31-May-01	218	80	04-Jun-01	222	60
12-Nov-00	18	80	13-Nov-00	19	70	01-Jun-01	219	80	05-Jun-01	223	60
17-Nov-00	23	80	17-Nov-00	23	60	02-Jun-01	220	90	07-Jun-01	225	40
21-Nov-00	27	90	20-Nov-00	26	70	05-Jun-01	223	70	08-Jun-01	226	80
28-Nov-00	34	80	28-Nov-00	34	80	06-Jun-01	224	70	09-Jun-01	227	70
02-Dec-00	38	70	04-Dec-00	40	60	07-Jun-01	225	80	11-Jun-01	229	50
05-Dec-00	41	70	06-Dec-00	42	60	08-Jun-01	226	70	13-Jun-01	231	80
10-Dec-00	46	60	09-Dec-00	45	140	10-Jun-01	228	60	14-Jun-01	232	70
12-Dec-00	48	60	13-Dec-00	49	110	11-Jun-01	229	70	17-Jun-01	235	40
17-Dec-00	53	150	15-Dec-00	51	90	12-Jun-01	230	80	18-Jun-01	236	120
21-Dec-00	57	130	20-Dec-00	56	80	14-Jun-01	232	80	19-Jun-01	237	90
23-Dec-00	59	110	22-Dec-00	58	80	16-Jun-01	234	80	20-Jun-01	238	70
26-Dec-00	62	100	25-Dec-00	61	70	17-Jun-01	235	150	21-Jun-01	239	60
29-Dec-00	65	90	29-Dec-00	65	60	20-Jun-01	238	130	22-Jun-01	240	50
31-Dec-00	67	90	30-Dec-00	68	60	21-Jun-01	239	120	23-Jun-01	241	120
03-Jan-01	70	80	05-Jan-01	72	70	22-Jun-01	240	110	24-Jun-01	242	100
05-Jan-01	72	70	07-Jan-01	74	60	23-Jun-01	241	100	25-Jun-01	243	70
10-Jan-01	77	70	12-Jan-01	79	60	24-Jun-01	242	90	26-Jun-01	244	50
13-Jan-01	80	80	14-Jan-01	81	50	25-Jun-01	243	95	27-Jun-01	245	40
15-Jan-01	82	90	17-Jan-01	84	50	26-Jun-01	244	90	28-Jun-01	246	110
19-Jan-01	86	80	19-Jan-01	86	50	27-Jun-01	245	90	29-Jun-01	247	90
23-Jan-01	90	80	23-Jan-01	90	140	28-Jun-01	246	100	30-Jun-01	248	80
26-Jan-01	93	70	25-Jan-01	92	120	29-Jun-01	247	95	01-Jul-01	249	60
28-Jan-01	95	70	28-Jan-01	95	100	30-Jun-01	248	90	02-Jul-01	250	50
30-Jan-01	97	60	31-Jan-01	98	90	01-Jul-01	249	90	03-Jul-01	251	40
03-Feb-01	101	60	03-Feb-01	101	80	02-Jul-01	250	90	04-Jul-01	252	120
07-Feb-01	105	60	08-Feb-01	106	70	03-Jul-01	251	85	05-Jul-01	253	100
10-Feb-01	108	60	10-Feb-01	108	60	04-Jul-01	252	80	06-Jul-01	254	80
12-Feb-01	110	50	13-Feb-01	111	60	05-Jul-01	253	75	07-Jul-01	255	70
15-Feb-01	113	60	16-Feb-01	114	50	06-Jul-01	254	80	08-Jul-01	256	60
19-Feb-01	117	60	19-Feb-01	117	50	07-Jul-01	255	75	09-Jul-01	257	40
20-Feb-01	118	160	21-Feb-01	119	60	08-Jul-01	256	80	10-Jul-01	258	100
22-Feb-01	120	140	23-Feb-01	122	50	09-Jul-01	257	85	11-Jul-01	259	70
23-Feb-01	121	130	27-Feb-01	126	50	10-Jul-01	258	70	12-Jul-01	260	60
26-Feb-01	124	100	03-Mar-01	129	130	11-Jul-01	259	70	13-Jul-01	261	50
02-Mar-01	128	90	08-Mar-01	134	100	12-Jul-01	260	60	14-Jul-01	262	110
04-Mar-01	130	80	11-Mar-01	137	90	13-Jul-01	261	70	15-Jul-01	263	90
07-Mar-01	133	70	13-Mar-01	139	80	14-Jul-01	262	60	16-Jul-01	264	70
11-Mar-01	137	80	17-Mar-01	143	70	15-Jul-01	263	70	17-Jul-01	265	60
14-Mar-01	140	60	19-Mar-01	145	60	16-Jul-01	264	150	18-Jul-01	266	50
16-Mar-01	142	80	22-Mar-01	148	50	17-Jul-01	265	140	19-Jul-01	267	40
19-Mar-01	145	80	23-Mar-01	149	40	18-Jul-01	266	130	20-Jul-01	268	120
21-Mar-01	147	90	25-Mar-01	151	140	19-Jul-01	267	120	21-Jul-01	269	100
23-Mar-01	149	70	29-Mar-01	155	110	20-Jul-01	268	110	22-Jul-01	270	80
25-Mar-01	151	60	30-Mar-01	156	100	21-Jul-01	269	100	23-Jul-01	271	70
26-Mar-01	152	60	31-Mar-01	157	90	22-Jul-01	270	90	24-Jul-01	272	60
27-Mar-01	153	150	01-Apr-01	158	80	23-Jul-01	271	100	25-Jul-01	273	40
28-Mar-01	154	140	04-Apr-01	161	80	24-Jul-01	272	100	26-Jul-01	274	120
30-Mar-01	156	120	05-Apr-01	162	70	25-Jul-01	273	90	27-Jul-01	275	110
09-Apr-01	166	90	09-Apr-01	166	60	26-Jul-01	274	90	28-Jul-01	276	90
10-Apr-01	167	80	11-Apr-01	168	60	27-Jul-01	275	80	29-Jul-01	277	80
11-Apr-01	168	90	13-Apr-01	170	50	28-Jul-01	276	80	30-Jul-01	278	70
13-Apr-01	170	90	15-Apr-01	172	50	29-Jul-01	277	90	31-Jul-01	279	60
14-Apr-01	171	90	16-Apr-01	173	40	30-Jul-01	278	80	01-Aug-01	280	120
15-Apr-01	172	80	20-Apr-01	177	120	31-Jul-01	279	80	02-Aug-01	281	100
16-Apr-01	173	80	21-Apr-01	178	100	01-Aug-01	280	90	03-Aug-01	282	90
18-Apr-01	175	80	22-Apr-01	179	90	02-Aug-01	281	150	04-Aug-01	283	70
21-Apr-01	178	80	23-Apr-01	180	80	03-Aug-01	282	140	05-Aug-01	284	60
22-Apr-01	179	70	24-Apr-01	181	80	04-Aug-01	283	130	06-Aug-01	285	40
23-Apr-01	180	70	27-Apr-01	184	70	05-Aug-01	284	120	07-Aug-01	286	110
24-Apr-01	181	80	28-Apr-01	185	60	06-Aug-01	285	100	08-Aug-01	287	90
25-Apr-01	182	80	29-Apr-01	186	70	07-Aug-01	286	90	09-Aug-01	288	70
28-Apr-01	185	70	30-Apr-01	187	50	08-Aug-01	287	85	10-Aug-01	289	50
29-Apr-01	186	80	01-May-01	188	40	09-Aug-01	288	90	11-Aug-01	290	120
30-Apr-01	187	70	04-May-01	191	120	10-Aug-01	289	90	12-Aug-01	291	90
01-May-01	188	80	05-May-01	192	100	11-Aug-01	290	85	13-Aug-01	292	70
02-May-01	189	70	09-May-01	196	70	12-Aug-01	291	85	14-Aug-01	293	50
05-May-01	192	70	13-May-01	200	40	13-Aug-01	292	80	15-Aug-01	294	110
06-May-01	193	60	14-May-01	201	110	14-Aug-01	293	80	16-Aug-01	295	80
07-May-01	194	60	15-May-01	202	90	15-Aug-01	294	75	17-Aug-01	296	60
10-May-01	197	60	17-May-01	204	80	16-Aug-01	295	70	18-Aug-01	297	40
12-May-01	199	70	18-May-01	205	70	17-Aug-01	296	75	19-Aug-01	298	110
14-May-01	201	50	19-May-01	206	60	18-Aug-01	297	70	20-Aug-01	299	90
15-May-01	202	60	20-May-01	207	60	19-Aug-01	298	60			
16-May-01	203	60	21-May-01	208	50	20-Aug-01	299	65			
18-May-01	205	140	23-May-01	210	40	21-Aug-01	300	60			
19-May-01	206	130	24-May-01	211	100	22-Aug-01	301	60			
20-May-01	207	120	26-May-01	213	80	23-Aug-01	302	60			
21-May-01	208	110	27-May-01	214	70						