

THE PERFORMANCE OF A SEQUENCING BATCH REACTOR FOR THE  
TREATMENT OF WHITEWATER AT HIGH TEMPERATURES

by

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## ABSTRACT

Environmental and economic pressures on pulp and paper mills have prompted the adoption of water-reducing strategies such as whitewater system closure. Efforts to reduce water use in the whitewater system increase the whitewater temperature and cause operational and quality problems in the papermachine through the build-up of dissolved contaminants in the whitewater. To control the build-up of dissolved and colloidal substances in the whitewater, an aerobic bioreactor is proposed to treat a substream of the closed whitewater loop.

This research investigated the biological treatability of a synthetic closed-system whitewater at high temperatures with an aerobic biological sequencing batch reactor (SBR), focusing on the removal of resin and fatty acids, one of the problem compound groups. The bioreactor was operated at a hydraulic retention time (HRT) of 2 days and a solids retention time (SRT) of over 15 days with the intention of maintaining a viable biomass at a mixed liquor volatile suspended solids (MLVSS) level between 2000 and 5000 mg/L. The performance of the bioreactor was assessed at 20, 30, 40, 45, and 50°C in terms of total dissolved solids (TDS), total organic carbon (TOC), chemical oxygen demand (COD), and resin and fatty acid (RFA) removal.

The removal of conventional contaminants such as TDS, TOC, and COD was significant at temperatures up to and including 40°C while at higher temperatures, contaminant removal was reduced. Parameters describing reactor operation and performance such as the food to microorganism ratio, the specific substrate utilization rate, and growth yield indicated a reduced conventional contaminant removal capability at temperatures higher than 40°C, along with a decrease in reactor biomass inventories at the higher temperatures.

The removal efficiencies of fatty acids (FA) were over 95% at all temperatures, but for resin acids (RA), near-complete removal was observed only up to 40°C. At higher temperatures, the removal efficiencies of RA were reduced, but still significant. Measurements during the SBR react cycle indicated that FA were mainly associated with the suspended solids, while RA were associated with both the liquid and solid phases. Observed specific removal rates decreased with increasing temperature, while maximum specific removal rates were high for all temperatures studied. For FA, the maximum removal rates were about twice the observed removal rates, while for RA, the maximum removal rates were about four times the observed removal rates. The FA content in the biomass appeared to decrease with increasing temperature, while the RA content appeared to increase. The RFA removed did not accumulate on the suspended solids because the RFA content in the biomass was negligible compared to the overall mass flow through the system. A large non-RFA extractable, chromatographable component of material was removed at all temperatures, though less removal was observed at 50°C.

Overall, the bioreactor performed best at temperatures below 40°C for the removal of both conventional contaminants and RFA, especially, RA. These experiments indicated that the biological portion of the membrane bioreactor device would be able to control the concentrations of dissolved and colloidal material using feed from a closed-loop whitewater application. The problems encountered at higher temperatures such as low sludge growth, solids loss in the effluent, and substantial RA in the effluent would be reduced with the combination of an ultrafiltration unit. Thus, treatment using the membrane bioreactor would probably be effective at temperatures higher than 40°C.

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## ABBREVIATIONS

ANAMET	Anaerobic - aerobic methane
BCTMP	Bleached chemical thermal mechanical pulping
BOD <sub>5</sub>	Biological oxygen demand (5-day)
CFS	Continuous flow system
COD	Chemical oxygen demand
CTMP	Chemical thermal mechanical pulping
DCOD	Dissolved chemical oxygen demand
DCS	Dissolved and colloidal substances
DHA	Dehydroabietic acid
EDTA	Ethylenediamine tetraacetate
Eff	Effluent
FA	Fatty acids
F/M	Food to microorganism ratio
HRT	Hydraulic retention time
ID	Internal diameter
Inf	Influent
ML	Mixed liquor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
PAPRICAN	Pulp and Paper Research Institute of Canada
QA/QC	Quality assurance, quality control
RA	Resin acids
RFA	Resin and fatty acids
SBR	Sequencing batch reactor
SRT	Solids retention time
TDS	Total dissolved solids
TCOD	Total chemical oxygen demand
Temp	Temperature
TMP	Thermal mechanical pulping
TOC	Total organic carbon
TSS	Total suspended solids
U	Specific substrate utilization rate
UASB	Upflow anaerobic sludge blanket
VFA	Volatile fatty acid
VSS	Volatile suspended solids
Y	Growth yield

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## **1. INTRODUCTION**

### **1.1. Motivation of Research**

Environmental and economical pressure on pulp and paper mills have prompted them to adopt water-reducing strategies. The whitewater system consumes a large proportion of water used in a mill. Efforts to use less water in the whitewater system have caused operational and quality problems in the papermachine through the build-up of dissolved contaminants in the whitewater.

This research investigated the treatability of a synthetic closed-system whitewater, focusing on the removal of resin and fatty acids, one of the problem compound groups. Since closed whitewater system would retain heat, the operating temperature would increase and the whitewater would have to be cooled before being treated. The higher the temperature the treatment system can operate at, the lower the costs of cooling the whitewater. Thus, this research investigated the treatment performance at varying temperatures.

### **1.2. Thesis Organization**

Chapter 2 gives background information and a literature review of subjects related to the membrane bioreactor research, including an elaboration on the motivation of this research and necessary background information on whitewater systems, closure, whitewater composition, whitewater treatment strategies, resin and fatty acid removal at high temperatures, and sequencing batch reactors. Chapter 3 describes the objectives of the research. Chapter 4 describes the materials and experimental methods used. Chapter 5 presents and discusses the results from this research. Lastly, chapter 6 lists conclusions and recommendations for future research. The appendices contain information on calculating certain parameters (Appendices A and B), report extra results (Appendix C), and present the raw experimental data (Appendix D).

## **2. BACKGROUND AND LITERATURE REVIEW**

### **2.1. Introduction**

The pulp and paper industry uses large quantities of water in its processes. As environmental and economic pressures limit the amount of water available, the industry is working to reduce water consumption. Closing mills through containment and re-use of liquid offers a possible approach to limit fresh water use and wastewater discharge. Although partial closure strategies have been applied successfully to other pulping processes such as in kraft and sulphite mills, a prime candidate for mill closure is the integrated mechanical newsprint mill because its water consumption is mainly in the papermaking process whereas other processes consume significant amounts of water in the bleaching plant or in the chemical pulping process.

#### **2.1.1. Water Use in Mechanical Newsprint Mills**

Pulp and paper processing uses large quantities of water in integrated mechanical mills to flush out contaminants resulting from normal operations. Older mechanical mills especially, designed to use this strategy of contaminant management, use from 50 to 200 m<sup>3</sup>/adt of water (Wearing, 1992). Even new mechanical pulping configurations are designed for 10 to 20 m<sup>3</sup>/adt of fresh water consumption. Large water requirements for mills require a substantial available water supply, restricting the potential locations of mills.

With these high levels of water use, the most economical form of treating the water is a wastewater treatment plant that usually uses aerated biological systems to deal with the contaminants derived from the mill processes (Wearing, 1992, 1993a). These "end-of-the-pipe" treatment plants require large capital investments, substantial land areas for the treatment and for sludge landfill, a limited asset in coastal mountainous areas, and a receiving water body that can assimilate the flow of treated effluent. Thus, efforts to reduce water consumption and subsequent treatment are of interest to the industry.

Due to the trend to tighten environmental regulations and the competition for available water resources, this contaminant management strategy, requiring large quantities of fresh water that must be treated extensively before being returned to the environment, is becoming less feasible and less economical. An alternative approach to contaminant management is systems closure, allowing a reduction in water consumption, reducing the effluent volume, and opening up new liquid waste management options.

### **2.1.2. Systems Closure and Water Consumption Reduction**

Systems closure is an operation strategy that keeps uncontaminated water streams separated from contaminated streams and re-uses water in processes that might otherwise use fresh water. As well as conserving water, systems closure strategies reap other benefits such as fibre recovery, chemical recovery, and energy conservation. Disadvantages to closing process streams include capital implementation or adaptation costs and increased concentrations of materials in the process flows that could detract from process operation and product quality (Smook, 1982). Thus, if its problems can be solved, systems closure, as well as being advantageous environmentally by cutting down on liquid discharges, can gain savings from better operation efficiency.

One water-reducing strategy is to eliminate the need for an "end-of-the-pipe" biological treatment system through alternative liquid waste management strategies. At current water usages between 10 and 20 m<sup>3</sup>/adt, external biotreatment systems are the most cost-effective (Wearing, 1992, 1993a). At these water usages, concentration through evaporation of the liquid wastes is expensive because of the large amount of energy required for concentration, but this expense decreases as the total water usage decreases. Below current levels of water use, increased contaminant concentrations in the mill detract from product quality and overload aerobic biological treatment systems. However, if water use can be reduced to between 2 to 5 m<sup>3</sup>/adt, other waste management strategies become financially competitive

with biotreatment such as concentration, evaporation, and incineration, allowing a further reduction in water use (Wearing 1992, 1993a).

The increased contaminant concentrations in the process flows resulting from systems closure can be dealt with through various management strategies. Fibres and fines and other solids can be recovered through savealls, filters and screens. Options for the management of the dissolved and colloidal constituents of the process flows include chemical additives, filtration or local specialized biological treatment.

One of the principles of systems closure is the segregation of flows similar in characteristics to prevent contamination of a cleaner flow by a dirtier flow. Although final flows from different parts of the mill cannot be definitely characterized as "cleaner" or "dirtier", they have different characteristics, properties and contaminants, perhaps requiring different reclamation strategies. Thus, concentrating separately on different general processes in a mill such as pulping, washing or papermaking keeps contaminated water with similar characteristics together. The whitewater system is one such process that can benefit from systems closure strategies.

### **2.1.3. Whitewater Recycling**

In mechanical pulping processes, the whitewater system in the paperforming process uses a large proportion (Figure 1) of total mill water and thus efforts on reducing water usage in this part of the mill help reduce overall water usage towards the 2 to 5 m<sup>3</sup>/adt level. Whitewater is produced in the forming and dewatering of the fibre mat during paper formation. Material in the incoming pulp is dissolved, suspended or colloided into the whitewater as the whitewater suspends the pulp, then drains, forming the paper sheet. Whitewater can be re-used to a certain extent, but only up to a point at which the concentration of materials and contaminants in the water build up and start adversely affecting product quality and process

operations (Figure 2). Further recycling of whitewater within the papermaking system or in other processes requires some form of treatment to remove suspended, dissolved, and colloidal materials from the liquid.

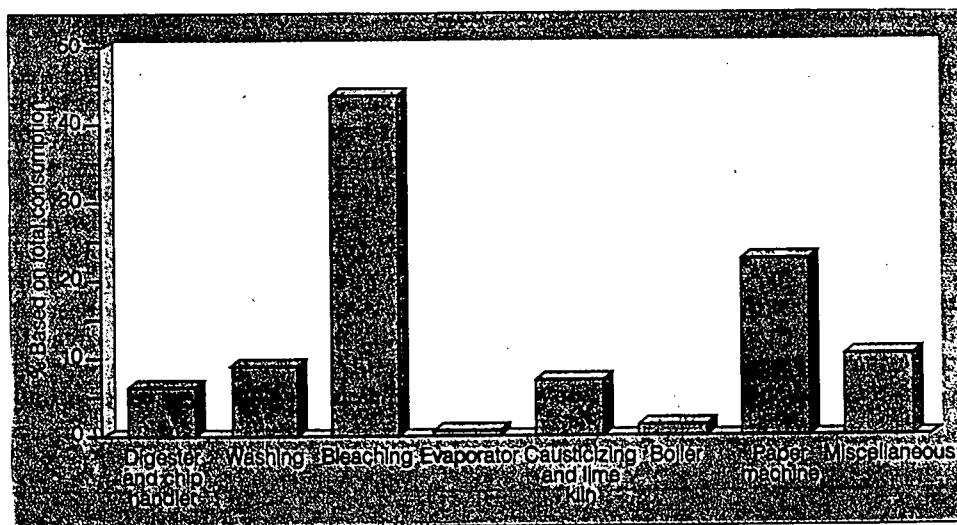


Figure 1. The consumption of water in the papermachine is a significant proportion of total mill water use. This breakdown of water use is for an alkaline pulping process (taken from Panchapakesan, 1992). An integrated mechanical newsprint mill would have water use reductions in pulping or digesting, in causticizing and lime kiln and in bleaching, and thus the water use of the papermachine would be an even higher proportion than shown in this bar graph.

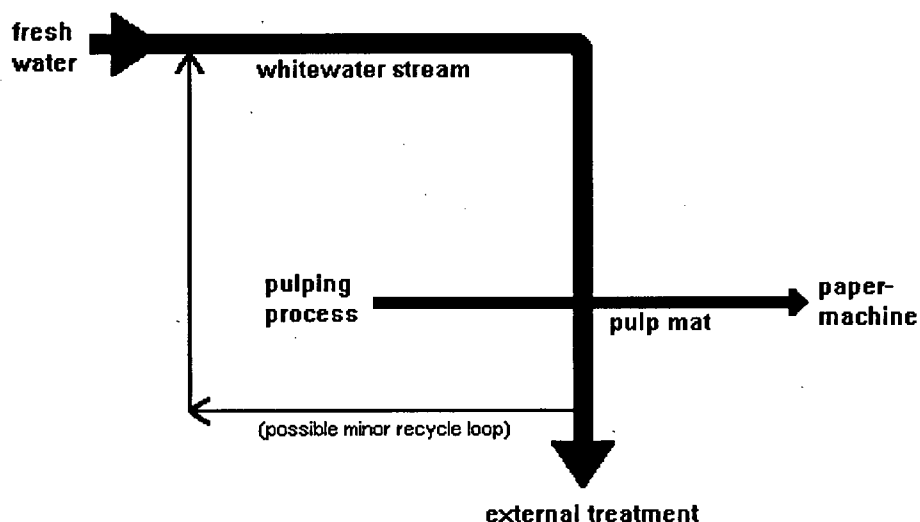


Figure 2. Whitewater configuration in a pulp mill with minimal recycling.

#### 2.1.4. Whitewater Treatment

The increased concentrations of suspended, dissolved, and colloidal substances in whitewater as a result of increased recycling must be controlled through some form of treatment. Biological treatment as a possible component of a membrane bioreactor process, is the strategy investigated in this research. This and other possibilities are discussed in Section 2.2.4.

Local biological treatment combined with ultrafiltration has been suggested as a possible strategy for removing contaminants from mill streams (Gerbas *et al.*, 1993). Since whitewater flows are much too large to treat biologically or with a membrane, a substream of the whitewater recycle loop could be treated first with a form of aerobic biological treatment

followed by an ultrafiltration membrane. The treated substream would be reintroduced to the whitewater flow, reducing the contaminant concentration to manageable levels (Figure 3). This would reduce the amount of fresh water make-up in the whitewater system.

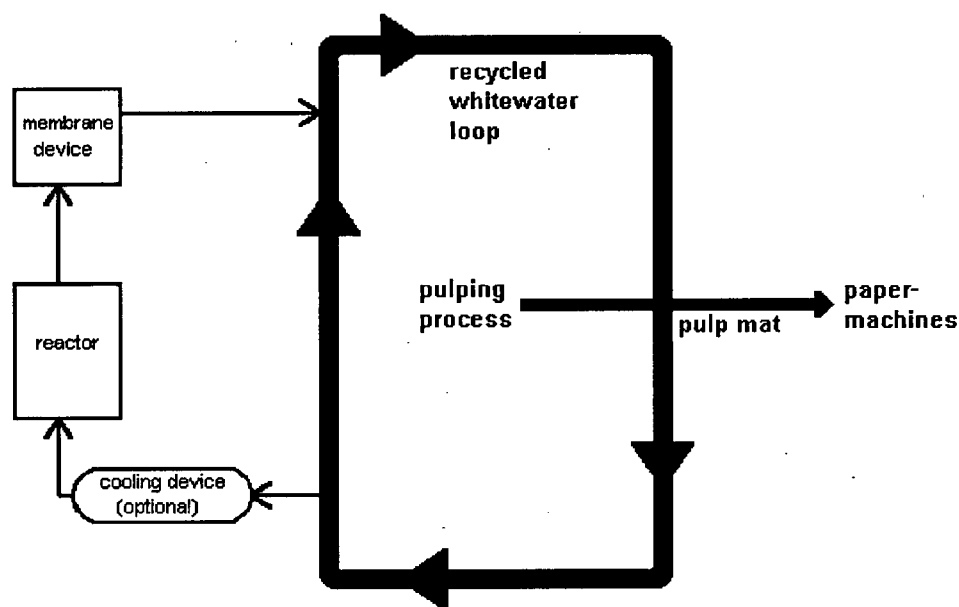


Figure 3. The proposed whitewater configuration with membrane bioreactor.

This treatment system would allow closure of the whitewater loop. As a result, heat would be trapped within, raising the overall temperature of the whitewater to about 70°C (Wearing, 1993b). Since biological systems do not operate well at such high temperatures and membrane devices have upper temperature operation limits, the substream would have to be cooled before being treated, an expensive adjustment. Thus, efficient operation of this treatment system at the highest temperature possible would minimize cooling costs.

Ultrafiltration by itself under high recycle conditions would produce a highly toxic waste concentrate stream. In addition, under high recycle conditions, membrane fouling might be a problem. Biological treatment by itself might not remove enough material to keep contaminant levels within the whitewater system low enough to avoid problems in product production. In addition, the growth of fungi and bacteria within the whitewater system might be enhanced by a seed population escaping from the biological treatment process and biocides and slimicides could not be used because they would reduce the viability of the treatment biomass.

By combining both technologies, the contaminant removals from each technology could complement and add to each other. Ideally, the biological treatment would control the contaminant levels within the treatment system, containing the solids through clarification, or, in the case of a sequencing batch reactor, in a settling stage. The containment of residual biomass and contaminants could be further enhanced by the ultrafiltration membrane.

To better understand the potential for this contaminant management strategy, backgrounds in the whitewater system and the composition of whitewater are useful.

## **2.2. Whitewater System**

The whitewater system is the network of flows from different areas in the papermaking process. The papermaking process occurs after the wood chips have been pulped and the pulp has been cleaned. Whitewater is the process water that is used in the suspension and drainage during the formation of the paper sheet.

### **2.2.1. Current Whitewater System Configuration**

Current "traditional" whitewater systems use large flows of fresh water to flush out contaminants and to ensure optimal sheet formation. Figure 4 illustrates the papermaking



whitewater process flows of a relatively open newsprint machine. Figure 5 shows the water balance for the whitewater system shown in Figure 4. Even though a large proportion of the whitewater is recycled, whitewater must be sewerred from the system to make way for the freshwater input into the system in sealing water for pumps and mixers, shower water in the fourdrinier and press components, cooling and sealing water for vacuum pumps, and cooling water in the drying component. By removing whitewater, contaminant levels are controlled through flushing out, but the loss of the hot whitewater means an energy loss from the system (Smook, 1982).

The whitewater system can be "closed" by using equipment that requires less water and by collecting, segregating and re-using cleaner whitewater streams and cooling waters and by reclaiming filler and fibre through savealls and filters (Wearing *et al.*, 1985; Smook, 1982). Figure 6 shows the flows of a closed whitewater system. The problems associated with the closure of the whitewater system will be discussed in more detail in section 2.2.3. In order to understand the impact of closing the whitewater system, the composition of whitewater must be understood.

### **2.2.2. Composition of Whitewater**

In integrated thermomechanical pulping (TMP) newsprint mills, the whitewater contains fewer non-wood chemical additives than whitewater from other mills simply because the TMP process does not use large amounts of chemicals to pulp, such as does the kraft process. The composition of whitewater under present process configurations that do not utilize much recycling of whitewater, differs from the predicted composition of whitewater in closed systems where process configuration allows for considerable recycling.

#### **2.2.2.1. Composition of Whitewater Under Low-Volume Recycling Conditions**

Under present operation with low whitewater recycling, whitewater usually is composed of fines, fibres, and soluble organics. The soluble organics consist mainly of lignin, carbohydrates and extractives (Järvinen *et al.*, 1985). Even so, the suspended and dissolved solids composition of whitewater varies from mill to mill and is affected by the type of stock, the type of non-fibrous furnish, and degree of whitewater recycle.

Suspended solids content in the whitewater varies with the size of the wire, the quantities of additives added in paper formation, the amount of suction used on the wet sheet, the machine speed, the grade of paper being produced, and the amount of whitewater recycled (Springer and Peterson, 1980). Suspended solids can be removed from the flow by using flotation savealls or disc filters, so, in effect, their concentrations can be controlled in low-recycle and high-recycle conditions (Smook, 1982).

#### **2.2.2.2. Composition of Whitewater under High-Volume Recycling Conditions**

Under greater recycling conditions, with the water leaving the system being reduced, the fibres and fines that are washed through the wire and are not recovered on filters might be recycled through the system again rather than being directly lost from the system. Thus, the concentration of fibre and fines in the whitewater would increase with increased closure, but filters would be able to recover much of this, keeping concentrations under control.

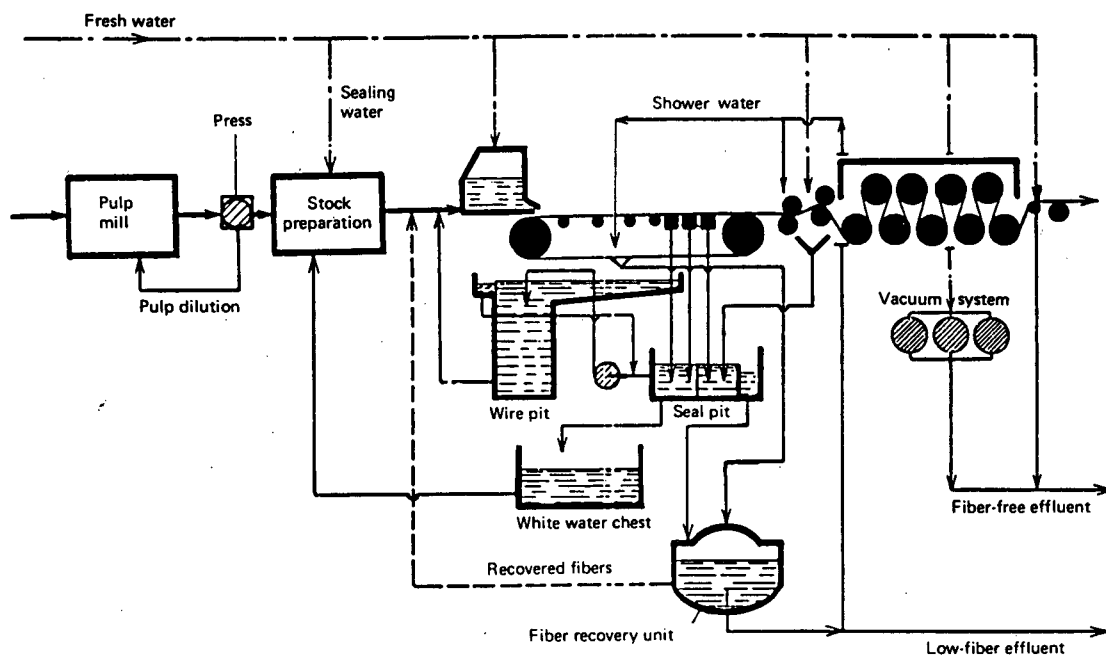
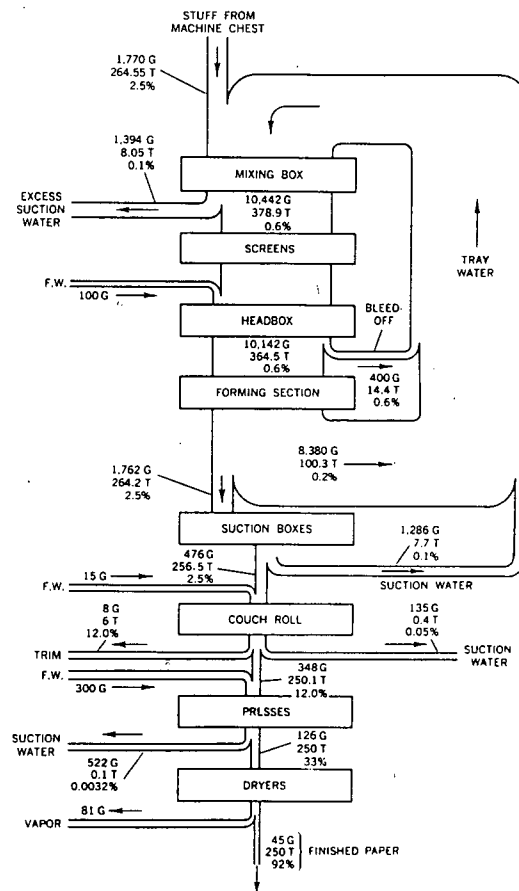


Figure 4. The paperforming whitewater process flows of a relatively open newsprint machine (taken from Smook, 1982).



F.W. = fresh water  
 G = gallons per min.  
 % = consistency, o.d.  
 T = tons/24/h, o.d.

Figure 5. The water balance for the whitewater system shown in Figure 4 (taken from Smook, 1982).

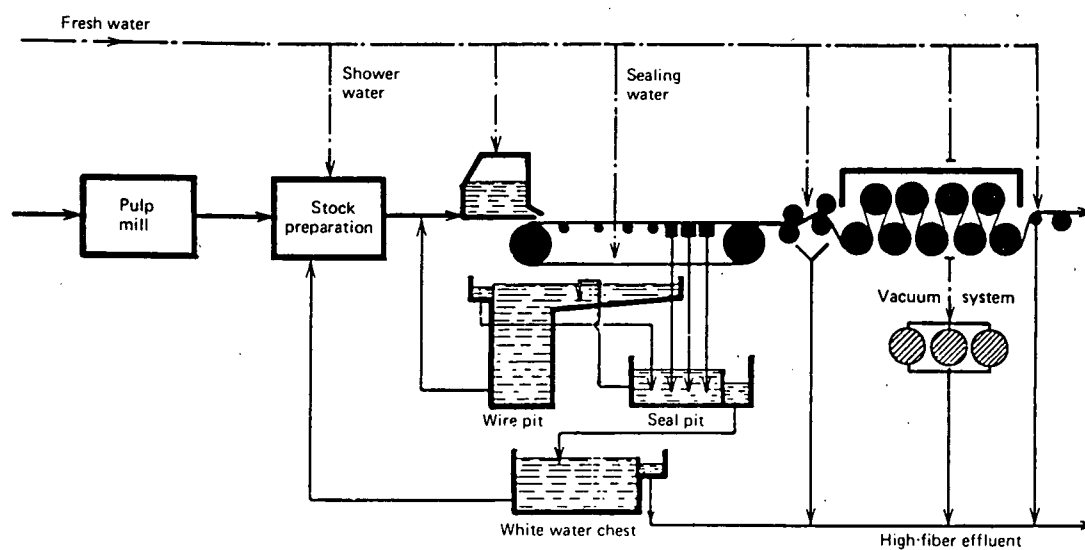


Figure 6. The flows of a closed whitewater system (taken from Smook, 1982).

As the recycling of whitewater is increased, the same materials that are dissolved from the pulp in low-recycle conditions will accumulate within the whitewater system. In addition to full-scale observations, laboratory studies using TMP newsprint pulp have demonstrated this relationship (Järvinen *et al.*, 1985) (Figures 7 and 8). The Pulp and Paper Research Institute of Canada (PAPRICAN) estimates that the total dissolved solids (TDS) concentration of a closed system whitewater could be between 3000 to 4000 mg/L (Wearing, 1993b). Specific problem compounds such as resin and fatty acids would increase in concentration unless they are removed somehow. The papermachine can tolerate resin and fatty acid concentrations of between 12 and 15 mg/L. Thus, a method of whitewater treatment would be required to keep the resin and fatty acid concentrations down to this level in the whitewater system (Wearing, 1993b).

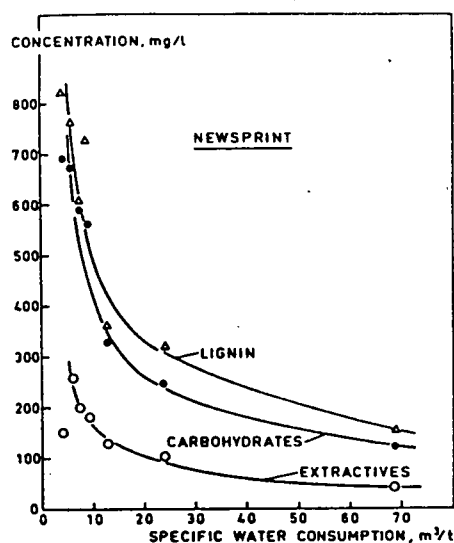


Figure 7. The dissolved components of whitewater increase in concentration as the recycling of whitewater is increased as indicated by a lower specific water consumption (taken from Järvinen *et al.*, 1985).

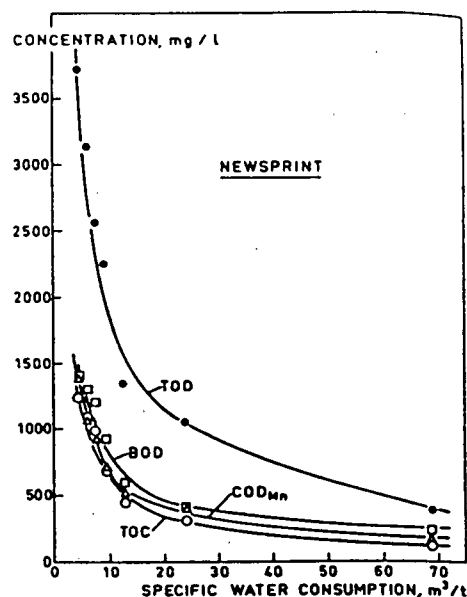


Figure 8. The oxygen demand of whitewater increases in concentration as the recycling of whitewater is increased as indicated by a lower specific water consumption (taken from Järvinen *et al.*, 1985).

As well as increased suspended and dissolved components in the whitewater, increased recycling would change the heat balance of the system. The amount of heat entering the system from the pulping process would remain the same, but the reduced or eliminated effluent flow would reduce heat loss by that avenue. In this case, either the temperature of the whitewater system would increase or heat losses would increase to compensate. At current water usages, papermachine temperatures range from 45 to 60°C (Panchapakesan, 1992). By closing the whitewater system, PAPRICAN estimates operating temperatures of 60 to 70°C would result (Wearing, 1993b). In any case, the probable predicted increase in whitewater temperatures should not cause problems in the papermaking process (Järvinen *et al.*, 1985). One advantage to a higher system temperature is an improvement in drainage (Smook, 1982; Springer and Peterson, 1980).

### **2.2.3. Problems Associated with Whitewater Closure**

As discussed in the section on the composition of whitewater under high-recycle conditions (Section 2.2.2.2.), suspended and dissolved solids concentrations would be high and temperature would increase. Table 1 lists the potential problems associated with whitewater closure and their causes. The most important of these are "plugging of wire and headbox showers and felt filling, corrosion, scale, foaming, slime, sizing and problems with colour and deposits." (Springer and Peterson, 1980)

#### **2.2.3.1. Suspended Solids Build-up**

Problems arise when the solids content of the whitewater affects the paper quality, such as may occur with a high content of fines (Springer and Peterson, 1980). The build-up of suspended solids composed of fibres, fines and additives can be managed through the strategic placement of clarification devices such as clarifiers, microstrainers, disc filters and flotation savealls (Smook, 1982; Springer and Peterson, 1980).

#### **2.2.3.2. Dissolved and Colloidal Substances Accumulation**

The build-up of dissolved and colloidal substances poses a greater challenge in the management of the whitewater system. The increased dissolved and colloidal substance concentrations would result in more deposits and biological growth throughout the system, increased corrosion, and an increase in "detrimental substances" or "anionic trash" (Panchapakesan, 1992; Sundberg *et al.*, 1993).



Table 1. The potential problems associated with whitewater closure are listed by cause (adapted from Springer and Peterson, 1980). An asterisk signifies importance.

Dissolved Solids Build-up	Suspended Solids Build-up	Temperature Increase
*Slime *Foam *Pitch *Corrosion *Sizing problems Product mottle *Colour pH control Precipitation *Scale Odour Deposits on paper Retention	Dirt Erosion Fines *Felt plugging *Wire plugging Wire life Felt life Reduced drainage rate *Headbox shower plugging	Temperature *Sizing problems Machine room temperature Reduced pumping capacity

If the conditions in the whitewater system are conducive to precipitation, deposits or scales can form on equipment exposed to whitewater. Inorganic anions such as carbonate, silicate, and sulfate can combine with cations such as calcium, magnesium, manganese, iron, aluminum and barium to form a precipitate. The precipitate might clog equipment or restrict flow. Controlling the hardness of the water controls the extent of deposits. However, under high whitewater recirculation conditions, this might not be feasible. In this case, sequestering or

dispersing agents such as ethylenediamine tetraacetate (EDTA) or organic polyelectrolytes can be used to reduce deposits (Springer and Peterson, 1980).

Similarly, certain conditions such as high nutrient and organics concentrations typical to highly closed systems promote biological growth within the whitewater system. Biological growth can result in slime deposits within the whitewater system and on the paper, and odour problems within the whitewater system. Typically, regular cleaning of equipment and the addition of biocides to the process water are used to control this problem (Springer and Peterson, 1980; Geller and Göttching, 1982). However, if the method of managing whitewater involves a biological reactor, biocides would inhibit the biological treatment. Thus, biological growth within the whitewater system would have to be controlled by alternate means.

Due to the changed conditions in a closed system, corrosion problems might become more of an issue. Under aerobic conditions, corrosion is usually caused by electrolytic factors and is affected by numerous variables such as dissolved oxygen concentration, acidity, temperature, surface flow velocity, carbon dioxide concentration, and the contact of metals that are different galvanically. To control corrosion, the pH can be adjusted, metals can be protected through cathodic installations, metal surfaces can be replaced with more similar metals to those used in the rest of the system, and protective coatings can line metal surfaces (Springer and Peterson, 1980).

Corrosion can also occur due to biological influences under anaerobic conditions in which sulfate-reducing bacteria can utilize cathodic hydrogen, reducing its impediment on corrosion (Springer and Peterson, 1980). Any kind of biological growth, aerobic or anaerobic, will allow the metal surfaces below the growth to become an anode, causing localized corrosion (Geller and Göttching, 1982). To control corrosion caused by anaerobic or aerobic bacteria,

biocides are used (Springer and Peterson, 1980). Care must be taken that the use of biocides does not adversely affect the researched biological whitewater treatment method.

With increased dissolved substances concentrations, the wet-end chemistry could also be affected. During paper formation, cellulosic materials must be bound to each other and any fillers must be incorporated into the paper structure. In general, fibres and most filler materials are anionic and repel each other. Thus, to promote strong interfibre bonding, cationic retention aids characterized by their high molecular weight and low charge density are added that act as bridges between fibres and between fibres and fillers, assisting in the formation of paper (Lindström *et al.*, 1974; Brouwer, 1991; Alince and Pikulik, 1991).

Increased concentrations of dissolved and colloidal substances (DCS) in whitewater affect the activity of these added retention aids. The DCS that interfere with retention action by tying up the retention aid are called "detrimental substances". Anionic DCS that interfere with retention aids are called "anionic trash" (Sundberg *et al.*, 1993). Although not completely identified, "detrimental substances" consist of dissolved and colloidal substances such as inorganic salts, mono- and oligosaccharides, lignins and lignin derivatives, humic acids and, more important to this research, resin and fatty acids and fatty acid esters (Welkener *et al.*, 1993). Papermachine runnability and paper quality can also be affected adversely by "detrimental substances" (Sundberg *et al.*, 1993). Thus, as whitewater closure increases and the dissolved and colloidal substance concentrations increase, "detrimental substances" become more of a problem in paper formation. To counteract this effect, additional retention aid can be added to compensate for the "detrimental substances" and other chemicals can be added to tie up the "detrimental substances" so that they do not interfere (Auhorn and Melzer, 1979).

Many of the solutions to these problems of scaling, biological growth, corrosion and "detrimental substances" involve adding chemical agents. If the whitewater system includes a biological treatment step, care must be taken in assessing the effects of these additives on the biological system. Biocides are obviously detrimental to a biological treatment system but slimicides or localized oxidizing agents might be used within the whitewater system without adversely affecting biological treatment. Slimicides act simply to detach biological growth from surfaces and thereby clean the contaminated area without killing the biological growth (Geller and Götsching, 1982). This would allow the biological growth to be contained within the biological reactor while controlling problems associated with the deposition and attachment of biological growth outside the biological reactor within the whitewater system. An option to slimicide usage might involve the application of a biocide such as peracetic acid that locally oxidizes the problem area and then quickly breaks down into harmless compounds (Huster *et al.*, 1991).

#### **2.2.3.3. Effect on Paper Quality**

Closing the whitewater system might also affect paper quality. As mentioned previously, "detrimental substances" can cause deposition of "pitch" or agglomerations of resin and fatty acids and their esters on the paper. This interferes with paper strength, brightness, aesthetics and papermachine runnability (Welkener *et al.* 1993).

In addition to pitch deposits on the paper, other paper qualities such as strength, permeability and optical characteristics can be affected by increased whitewater recycling. Laboratory tests (Järvinen *et al.*, 1985) found that increased recycling of whitewater resulted in increased air permeability and decreased tensile strength. This was thought to be due to poor interfibre bonding and an increased fines content. The increased recycling had a greater impact on the optical characteristics such as a decrease in brightness. These effects of whitewater closure

would vary from mill to mill with different furnish use, different extents of recycling and different product manufacture (Geller and Götttsching, 1982).

Overall, increased closure of whitewater systems could have some deleterious effects. The increase in suspended solids can be managed through strategic placement and operation of various physical separating technologies. Increased concentrations of dissolved and colloidal materials in the whitewater system can result in scaling, biological growth, and corrosion. The chemistry of wet-end operations can be altered by increased concentrations of dissolved and colloidal substances, causing problems in paper formation and additional consumption of additives. The use of highly-recycled water in papermaking can result in a product of lower quality than otherwise.

#### **2.2.4. Possible Whitewater Treatment Techniques**

To control problems arising from whitewater loop closure, different whitewater treatment techniques have been adopted by different mills. The extent of the treatment required depends on how much the recycled whitewater affects paper quality and production and on whether the mill wants to steer away from an "end-of-the-pipe" biological treatment system. Some mills have found that system reconfigurations and stream segregation, or chemical additive treatment such as addition of biocides and chemical precipitants, can be sufficient to control the effects of whitewater closure. On the other hand, other plants require more extensive removal of dissolved, colloidal and suspended material, necessitating strategies such as biological treatment or membrane filtration.

##### **2.2.4.1. Biological Treatment**

###### **Aerobic**

Aerobic treatment is advantageous over anaerobic treatment in its absence of odour problems, in the preferred aerobic biodegradation of compounds characteristic of whitewater (Eriksson,

1985) and in its combination with contaminant removal through volatilization or chemical oxidation due to aeration (Geller and Götsching, 1982; Liu *et al.*, 1993).

Using specialized organisms such as white-rot fungi and yeasts, aerobic fermentors can remove simple and complex sugars and low-molecular-weight lignins from wastewaters and convert them to microbial protein, a marketable resource. When the aerobic fermentors were tested on a pilot plant scale on the whitewater system of a newsprint mill, using a residence time of 17 hours, organic materials did not accumulate within the whitewater system (Eriksson, 1985). By reducing the residence time by recirculating a fraction of the microbial protein, complete closure of a whitewater system in a large newsprint mill would require a reactor volume of 200-400m<sup>3</sup> (Eriksson, 1985). The microbial protein produced could either be marketed as livestock feed or added to the paper without affecting paper quality up to contents of 1.5%, equivalent to the sludge production of this process applied to a large newsprint mill (Eriksson, 1985). However effective and advantageous, aerobic biological treatment of whitewater has not been fully investigated because the need for biological whitewater treatment is relatively recent.

### **Anaerobic**

Anaerobic treatment, when compared to aerobic treatment, offers the advantages of high temperature tolerance, lower energy consumption, lower sludge production, and production of methane that can be used in the mill. However, the slow growth rate of anaerobic microorganisms, requiring a high solids retention time, might necessitate large treatment systems to deal with the large flow of whitewater. In addition, anaerobic treatment is not as efficient in contaminant removal as aerobic treatment (Tchobanoglous and Burton, 1991). Since lignins of molecular weight above 850 are degraded through oxidation, anaerobic treatment would not break down these compounds, allowing for compound build-up in the whitewater system (Eriksson, 1985; Rintala and Lepistö, 1992). These large lignin molecules

are usually coloured and would detract from paper whiteness if left to accumulate in the whitewater system (Eriksson, 1985). Effluents of anaerobic processes are quite unattractive due to their odor and anoxic properties (Frostell, 1983). The sensitivity of anaerobic treatment to contaminants toxic to the biomass, such as sulphur, might be detrimental to the treatment because of build-up of these and other inhibiting compounds in a closed whitewater system (Huster *et al.*, 1991). McCarthy *et al.* (1990) found that resin and fatty acids inhibited anaerobic biodegradation of bleached chemi-thermomechanical pulping (BCTMP) wastewater. However, anaerobic treatment has been investigated in the treatment of closed-system papermachine flows.

For example, anaerobic fluidized bed technology has been applied to closed whitewater situations (Johnstone *et al.*, 1995; Wendling *et al.*, 1994; Barascud *et al.*, 1993). Johnstone *et al.* (1995) found that for different treatment flows the COD (chemical oxygen demand) removal in a bench scale closed whitewater system ranged from 42 to 64%, from initial COD concentrations of 19 and 12.5 g/L respectively. This research has led to the industrial scale application of anaerobic fluidized bed treatment of a closed whitewater loop in the Lecoursonnois secondary fibre mill in France (Johnstone *et al.*, 1995).

Anaerobic thermophilic treatment of whitewater has the advantage of operating at temperatures similar to those of the whitewater system and higher loading rates combined with lower sludge wastage are characteristic of thermophilic operation over mesophilic (Rintala and Lepistö, 1992). Rintala *et al.* (1991) found 65 to 70% removal of COD at 55 and 65°C from a sulfate-rich TMP whitewater using laboratory-scale upflow anaerobic sludge blanket (UASB) reactors. The high sulfate content was thought to contribute 20-60% of the COD removal through sulfate reduction (Rintala *et al.*, 1991; Rintala and Lepistö, 1992). Subsequent high-temperature anaerobic treatment studies used semicontinuously fed batch digesters at 35, 55 and 65°C and UASB reactors at 55 and 70°C to treat TMP whitewater.

The UASB reactors removed 80% of the COD at 55°C and 60% at 70°C. While removing volatile fatty acids (VFAs) efficiently, the semicontinuously fed batch digesters removed the non-VFA component of COD only slightly and, at the higher temperatures, the non-VFA COD actually increased through treatment because of cell lysis. In any case, the food to microorganism (F/M) ratios for the semicontinuously fed batch digesters were 0.4, 0.6, and 0.7 g COD / g MLVSS·d (MLVSS = mixed liquor volatile suspended solids) for the reactors run at 35, 55 and 65°C respectively (Rintala *et al.*, 1991).

### **Combined Aerobic and Anaerobic Treatment**

Characteristic advantages and disadvantages are associated with the use of aerobic and anaerobic biological treatment. By using first anaerobic treatment then a follow-up aerobic treatment, the advantages of both treatments can be maximized. The low sludge yield for the organics removed for anaerobic treatment would allow economic organics removal. The following aerobic treatment would allow compounds not biodegradable anaerobically, to be removed aerobically, and odourous compounds produced during the anaerobic treatment could be oxidized during aerobic treatment, removing odour problems (Huster *et al.*, 1991).

Studies have investigated the integration of anaerobic and aerobic treatment stages and their application to the pulp mill industry. Theoretical assessments of the performance of combined anaerobic and aerobic treatments found them applicable and useful (Huster *et al.*, 1991). One such system, called the ANAMET (ANaerobic - Aerobic METHane) system, treated an influent of 50% whitewater and 50% chip washwater from a hardwood and softwood fibreboard mill (Frostell, 1983). Table 2 details the performances of the different treatment stages.

Although this system was designed for an "end-of-the-pipe" situation, its performance allows the possibility of being applied to a recirculated whitewater situation.



Table 2. The performances of the different treatment stages of ANAMET (compiled from Frostell, 1983) BOD<sub>5</sub> = Biological oxygen demand (5-day). Eff = Effluent. Inf = Influent.

Reactor Stage	Anaerobic	Aerobic	Overall
COD Inf [mg O <sub>2</sub> /L]	14600	8800	14600
COD Eff [mg O <sub>2</sub> /L]	8800	1700	1700
COD Removal [%]	40	81	88
BOD <sub>5</sub> Inf [mg O <sub>2</sub> /L]	6900	2500	6900
BOD <sub>5</sub> Eff [mg O <sub>2</sub> /L]	2500	210	210
BOD <sub>5</sub> Removal [%]	64	92	97
F/M [g BOD <sub>5</sub> / g MLVSS·d]	0.21	0.24	
Growth yield [g MLSS / g BOD <sub>5</sub> ]			0.17
Growth yield [g MLVSS / g BOD <sub>5</sub> ]			0.12

Additional research done by Rintala and Lepistö (1992) on a high-temperature aerobic stage that followed the thermophilic anaerobic treatments described earlier found an additional decrease in COD in the whitewater of 40% from the anaerobic effluent. The influent entering the 55°C anaerobic UASB reactor had a COD of about 3000 mg/L. After the anaerobic stage, the influent to the 55°C aerobic activated sludge treatment was between 1000 and 1500 mg COD/L. The final effluent exiting the aerobic treatment ranged from 500 to 1000 mg/L of COD (Rintala and Lepistö, 1992). This and previous examples show that combining anaerobic and aerobic treatments might be a feasible strategy for whitewater treatment.

#### 2.2.4.2. Membrane Treatments

Although membrane treatments do not break down organics as do biological treatments, their advantages are attractive. Since they rely on physical rather than biological means to concentrate and separate organics from aqueous streams, their operation might be less dependent on biologically-friendly conditions within the whitewater and a sufficiently constant supply of substrate. Membrane technologies might be disadvantageous in their potential for membrane fouling with resulting limitations in flows and loadings and in their requirement for treatment and ultimate disposal of concentrate.

A number of types of membrane technologies exists; some of which are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. These vary in their pore size and in the size of molecules that they can filter and in their operating pressure. Membrane technologies use a pressurized flow over the membrane, allowing some molecules to pass through the membrane and impeding others. The flow is separated into two streams, the permeate or the stream allowed through the membrane and the concentrate, the flow blocked by the membrane. Microfiltration is a membrane technology with a pore size in the micron range and is most useful in separating suspended solids from a flow (Zaidi *et al.*, 1991). Ultrafiltration blocks particles as small as 10 Å and reverse osmosis rejects particles as small as 1 Å including inorganic salts. Nanofiltration has a rejection size between ultrafiltration and reverse osmosis (Bryant and Sierka, 1993). These three membrane technologies have small enough pore sizes that many larger organic molecules are retained in the concentrate (Zaidi *et al.*, 1991; Bryant and Sierka, 1993). To reduce the potential for fouling, the water to be filtered should be pre-screened or pre-filtered to remove suspended solids (Bryant and Sierka, 1993; Paleologou *et al.*, 1993). Reverse osmosis can be used to treat the whitewater permeate for further purification if needed (Paleologou *et al.*, 1994).

#### 2.2.4.3. Ultrafiltration

Research on the ultrafiltration of whitewater resulted in 40 to 60% removal of COD, 60 to 100% removal of lignins, and a 50 to 90% reduction in cationic demand, similar to anionic trash discussed earlier, depending on the flow conditions. Two membranes were used, one made of polysulphone (PU 608 cutoff = 10kD) and the other of zirconium oxide coated carbon (M5 cutoff = 10kD). In addition, this study found that microorganisms at levels of 1,000,000/mL before filtration were reduced to 1,000/mL in the permeate (Nuortila-Jokinen *et al.*, 1994).

Another study examined the permeability of several ultrafiltration units made of polysulphones, hydrophilic polymer, cellulosic polymer on PVDF, or polyethersulphones to a solution of only dehydroabietic acid (DHA). Although DHA was much smaller than the filter pore sizes (ranging from 5 to 150 kD), it was retained in the concentrate. Since no larger molecules such as lignins or fibres were present for the resin acid to attach to, the study suggested that resin acids are retained through an interaction with the membrane (Zaidi *et al.*, 1991).

Prior to the present study, preliminary investigative work explored the behaviour of two ultrafiltration units made of polyethersulfone (MW cutoffs = 10 and 100 kD) at various temperatures on a synthetic whitewater used for the same biological treatment studies reported here (Elefsiniotis *et al.*, 1995). The membrane removal efficiencies for TDS, dissolved chemical oxygen demand (DCOD) and total organic carbon (TOC) from the synthetic whitewater were modest, ranging from 10 to 37%. Although resin acids were removed moderately at 25 to 45% removal, over 90% of the fatty acids were removed. Of the five major resin acids present (isopimaric, levopimaric + palustric, DHA and abietic), isopimaric and abietic exhibited the greatest rejection at about 50%, levopimaric + palustric were slightly lower at about 40% and DHA was quite low at 10% retention. The

investigation revealed that compound removal was not affected by operating temperatures ranging from 20 to 60°C.

#### 2.2.4.4. Biological Treatment Combined with Ultrafiltration

In addition to the ultrafiltration of synthetic whitewater, Elefsiniotis *et al.* (1995) ultrafiltered the effluent of one sequencing batch reactor (SBR) operating at 20 and 30°C and another identical SBR operating at 40°C. Table 3 summarizes the removals of various components from the biologically-treated effluent through two different ultrafiltration membranes.

Table 3. Percent removal of various parameters from biologically pre-treated whitewater by post-treatment with two types of ultrafiltration membranes (from Elefsiniotis *et al.*, 1995)  
Temp = Temperature.

Membrane Type	Temp. [°C]	TDS [%]	DCOD [%]	TOC [%]
M1	20	15	46	37
	30	9	50	41
	40	26	53	51
Mean		17	50	43
M2	20	21	72	65
	30	20	71	70
Mean		21	72	68

Again, operating temperatures ranging from 20 to 40°C did not affect removal efficiencies (Table 3). Figure 9 illustrates the removal contributions by the various treatment combinations, ultrafiltration alone, biological SBR treatment alone and ultrafiltration and

bioreactor combined at an operating temperature of 30°C. The biological SBR treatment data are presented and discussed in more detail in the Results and Discussion section (Section 5.). By combining ultrafiltration and aerobic biotreatment, 48% of the TDS was removed, 95% of the DCOD was removed, 93% of the TOC was removed, and 100% of the resin and fatty acids (RFAs) were removed from the synthetic whitewater (Elefsiniotis *et al.*, 1995). Although conditions imposed on the system were conservative, these results offer promise for the aerobic biological reactor coupled with an ultrafiltration membrane.

#### **2.2.4.5. Evaporation**

Evaporation is a separation technique that uses evaporation and condensation to purify process water. The slurry left after evaporation can be further concentrated and then incinerated. This process is used in the Millar Western Meadow Lake closed cycle BCTMP mill to manage mill liquid wastes. The initial condensates are "clean" at TDS concentrations of 150 mg/L, but as evaporation progresses, more volatiles condense with the water vapour. At Meadow Lake, 90% of the condensates are "clean" and the remaining 10% are less "clean" condensates containing 70% of the total volatile organics in the original process water (Gerbas *et al.*, 1993). Thus "clean" condensates and less "clean" condensates can be collected and reused for different purposes. Since this technology is used at Meadow Lake, practical experience has been gained and the technology has been proven in a full-scale situation. Application of this technology in aiding the closure of whitewater systems could be economically feasible in low water usage mills.

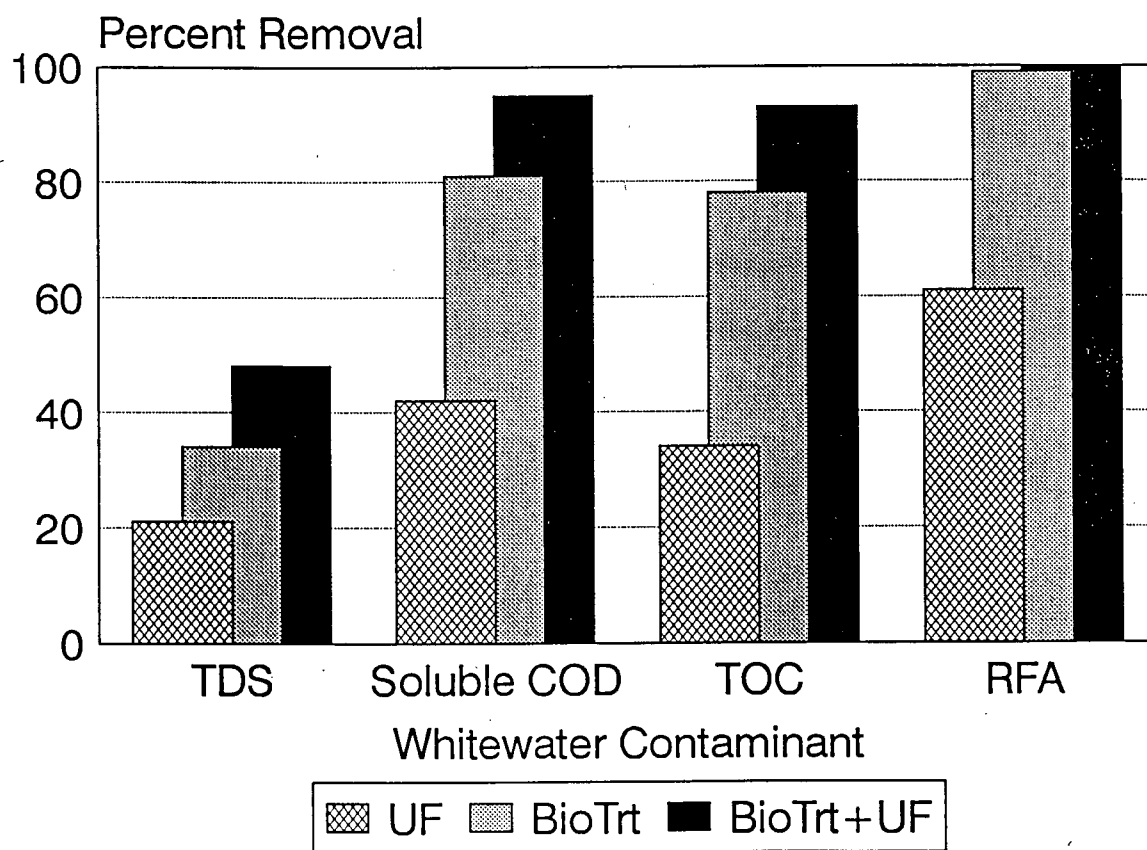


Figure 9. The percent removal of various components of the synthesized whitewater attributed to various components in the system, ultrafiltration alone, biological SBR treatment alone and ultrafiltration and bioreactor combined (taken from Elefsiniotis *et al.*, 1995).

#### **2.2.4.6. Freeze Crystallization**

Freeze crystallization is a separation process that uses slow careful cooling and removal of ice crystals from the contaminated water, leaving a more concentrated slurry to be evaporated and recovering water from the ice crystals. This technology was applied to the Louisiana-Pacific Canada mill in Chetwynd, B.C. but was abandoned because of problems with crystal size degradation and crystallizer tube icing with increased heat-transfer (Young, 1994). Unfortunately, the ice crystals can be contaminated by resin and fatty acids (Gerbasi *et al.*, 1993), defeating the water purification process needed in the whitewater system since resin and fatty acids have been found to be one of the problem compound groups involved in the closure of the whitewater system. Economically, freeze crystallization was found to be more expensive than biological treatment with ultrafiltration in an "end-of-the-pipe" mill situation with mill flows ranging from 5 to 20 m<sup>3</sup>/adt (Gerbasi *et al.*, 1993). For these reasons, freeze crystallization is most likely not appropriate in an application to whitewater system closure.

#### **2.2.4.7. Chemical Addition**

A number of chemicals are available for use in controlling problems caused by closure. Some, discussed earlier, control scaling, biological growth, or corrosion and others control pitch through precipitation and agglomeration (Smook, 1982). These methods are losing their main focus on problem management because the chemicals are expensive and might cause treatment problems later. Chemical addition is limited in its extent to deal with closure problems, increasing beyond its scope as the mill decreases water usage.

#### **2.2.4.8. Costs of Treatments**

Depending on the mill, its processes, the furnish and the final product, the problems encountered due to closure of the whitewater system vary from mill to mill and might be more extreme in certain mills over others. Some mills can get away with simply altering water usage to make it more efficient or using precipitation to control problems caused by dissolved

and colloidal substances. Others must make a greater investment in a more extensive treatment method in order to maintain adequate closed operation.

One investment forecast predicted the capital and operating costs of a biological membrane treatment, freeze crystallization, and evaporation in dealing with the liquid wastes of a closed TMP newsprint mill with a capacity of 550 adt/day. The study compared the alternative treatments to conventional activated sludge treatment with discharge at different water usage rates (Gerbasi *et al.*, 1993) (Table 4).

In examining the costs of these treatments, conventional biological treatment is still the cheapest even at low flows of  $5\text{m}^3/\text{adt}$ , but the operation costs reported assume that the sludge is marketable. Of the alternate treatments investigated, evaporation was the lowest in capital and operating costs, followed closely by the biological membrane treatment. Freeze crystallization was slightly more expensive in both capital and operating costs (Gerbasi *et al.*, 1993).

Another author estimated the prescreening and ultrafiltration capital costs to be \$5.8 million and the operating costs to be \$0.7 million/year for the treatment of mechanical pulp mill effluent at a water flow of  $5\text{m}^3/\text{adt}$  and a mill capacity of 550 adt/day, the same size mill as in Table 4 (Paleologou *et al.*, 1994). Evaporation and burning of all the liquid waste in the mill, not only the whitewater, could be financially competitive in energy costs with biotreatment at low water usages (Wearing, 1992). Combining reconfiguration of flows to maximize water use, ultrafiltration in the whitewater loop, and evaporation to concentrate the waste, the capital cost of building a closed-cycle system was somewhat more than a biological treatment system, the difference decreasing with lower water usage rates (Table 5) (Towers and Wearing, 1994).



Table 4. Estimated capital and operating costs for closed cycle options that do not produce effluent and conventional activated sludge secondary treatment that produces effluent for a 550 adt/day TMP newsprint mill at different water usage rates (Gerbas *et al.*, 1993). Cap = Capital costs. Op = Operating costs. \$M = Millions of 1992 Canadian dollars. \$M/y = Millions of 1992 Canadian dollars per year. The activated sludge operating cost at the 5 m<sup>3</sup>/adt flow has been credited with the income of marketing organic and inorganic dissolved solids.

Water Usage Rates	5 m <sup>3</sup> /adt		10 m <sup>3</sup> /adt		15 m <sup>3</sup> /adt		20 m <sup>3</sup> /adt	
Capital & Operating Costs	Cap	Op	Cap	Op	Cap	Op	Cap	Op
Treatment	\$M	\$M/y	\$M	\$M/y	\$M	\$M/y	\$M	\$M/y
Biological Membrane	19.3	0.71	28.1	2.21	36.8	3.28	44.0	4.19
Freeze Crystallization	23.3	0.83	33.9	2.27	52.6	3.55	63.2	4.44
Evaporation	18.0	0.55	26.5	2.03	34.8	3.04	42.6	3.91
Activated Sludge	11.1	0.00	11.5	0.70	11.9	1.00	12.3	1.20

Table 5. The capital and operating costs for the closure of an existing integrated newsprint mill at different water usage rates as compared to a conventional "end-of-the-pipe" biological treatment system (Towers and Wearing, 1994). M\$ = million Canadian dollars. /y = per year.

Effluent Processing Measures	Cost	
	Capital [M\$]	Operating [M\$/y]
Closed cycle without chemical regeneration		
10 m <sup>3</sup> /t	53	3.0
5 m <sup>3</sup> /t	43	1.4
2 m <sup>3</sup> /t	44	1.2
Closed cycle with chemical regeneration		
10 m <sup>3</sup> /t	62	0.7
5 m <sup>3</sup> /t	52	-0.9
2 m <sup>3</sup> /t	53	-1.1
Biological treatment and discharge		
30 m <sup>3</sup> /t	30	2.2

Even though these alternate treatments might be more expensive than biotreatment, their costs decrease as the water usage rates decrease, and advantages are gained in a closed system that cannot be measured financially. Further development of closed system waste management technologies might reduce the cost even more.

### 2.3. Potential Aerobic Treatability of a Closed Whitewater Stream

In order to assess the probable performance of a biological treatment process in the proposed closed-loop treatment alternative, a review of results of similar research is needed. Since interest in this type of technology is relatively new, very little research has been done on aerobic biotreatment of whitewater and its content of resin and fatty acids. More research has been done on the treatment of TMP and chemi-thermomechanical pulping (CTMP) effluents and their detoxification through effluent treatment by removing resin and fatty acids.

Conventional "end-of-the-pipe" treatment generally removes resin and fatty acids successfully given an adequate residence time (Leach *et al.*, 1977). One study monitored the removal of resin and fatty acids from TMP and CTMP effluent in an aerated lagoon. It was found that a 6-day residence time was required to remove toxicity due to resin and fatty acids. The initial resin acid concentrations were 17.07 mg/L for TMP and 41.72 mg/L for CTMP and the final resin acid concentrations were too low to detect for TMP and 1.13 mg/L for CTMP (Servizi and Gordon, 1986).

A group of researchers at the Université du Québec à Trois-Rivières have investigated the removal of resin and fatty acids along with other contaminants from CTMP effluent through laboratory-scale aerobic biotreatment in chemostats (Lo *et al.*, 1991). They varied parameters such as pH, hydraulic retention time (HRT) (and subsequently the solids retention time (SRT)), and dissolved oxygen (DO), while monitoring contaminant removal efficiencies for RFAs, BOD<sub>5</sub>, TOC, COD, and lignosulfonates (L.S.) (Figures 10, 11, and 12). The characteristics of the reactor influent, an effluent from CTMP washing, were: BOD<sub>5</sub> = 3000 mg/L, RFA = 45 mg/L, COD = 6200 mg/L, TOC = 1900 mg/L and LS = 2300 mg/L. Only two individual fatty acids were measured (linolenic and oleic) out of the five measured in the whitewater membrane bioreactor research. Reactor conditions varied around a pH of 7, an HRT of 2 days, a temperature of 20°C, and an aeration rate of 0.71 L/L·min. Optimum

removal efficiencies were observed at a pH of 7 and sludge settleability was good throughout the pH range tested. Removal efficiencies improved with increasing DO concentrations as did the mixed liquor suspended solids (MLSS) levels and the sludge settleability. However, the increase in RFA removal efficiencies observed with increasing aeration was insignificant. Below an HRT of 2 days, removal efficiencies decreased and HRTs greater than 2 days showed no further improvement in removal efficiencies. MLSS levels and settleabilities were high during all HRTs tested. In general, RFA removal efficiencies were not affected as much as the other characteristics measured.

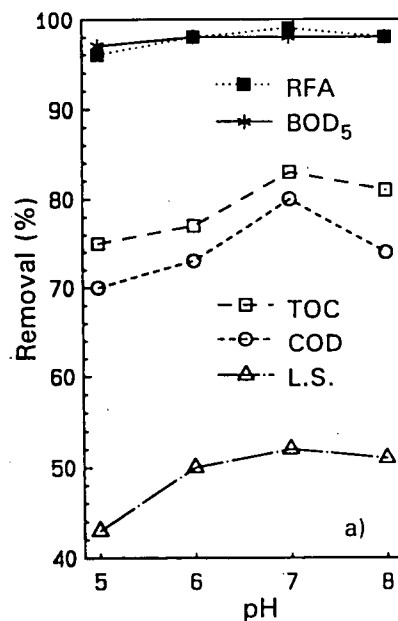


Figure 10. Contaminant removal efficiencies for RFAs, BOD<sub>5</sub>, TOC, COD, and lignosulfonates as functions of the pH (taken from Lo *et al.*, 1991).

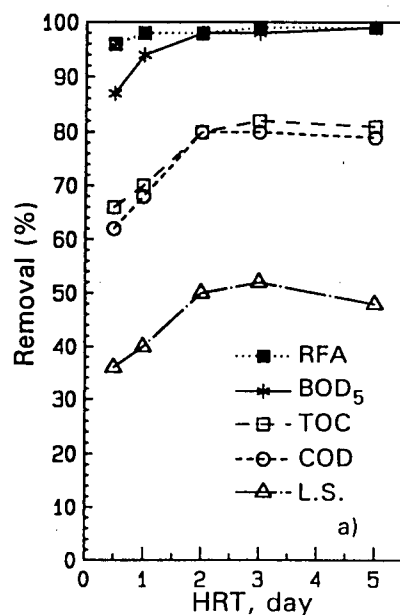


Figure 11. Contaminant removal efficiencies for RFAs, BOD<sub>5</sub>, TOC, COD, and lignosulfonates at varying HRTs (taken from Lo *et al.*, 1991).

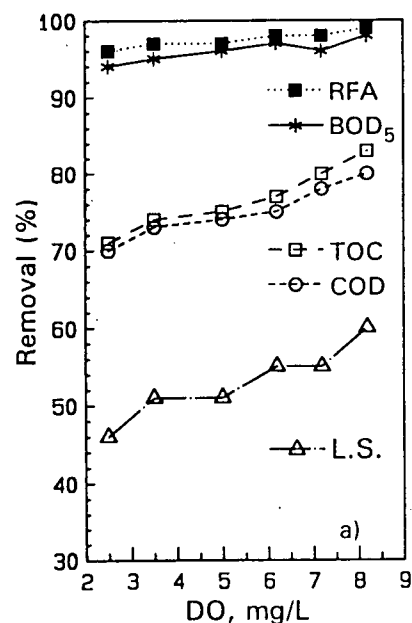


Figure 12. Contaminant removal efficiencies for RFAs, BOD<sub>5</sub>, TOC, COD, and lignosulfonates at varying dissolved oxygen concentrations (taken from Lo *et al.*, 1991).

## 2.4. High Temperature Aerobic Treatment of Resin and Fatty Acids

The other unique requirement for the membrane bioreactor treatment of whitewater is not only resin and fatty acid removal, but resin and fatty acid removal at high temperatures. In increasing the temperature, treatment can be compromised through less-efficient contaminant removal and problems with sludge settleability (Flippin and Eckenfelder, 1994).

Research performed by Lo *et al.* (1991) also included the monitoring of contaminant removal efficiencies with varying temperature (Figure 13). These results were the most noteworthy because of their implications to the present research on the biological stage of the membrane bioreactor for whitewater. RFA removal efficiencies decreased slightly as the temperature was increased from 20 to 50°C in 10° increments. Removal efficiencies for other parameters decreased somewhat from 20 to 40°C, and decreased significantly when the temperature was raised to 50°C. The increasing temperatures affected the MLSS levels similarly, decreasing them as the temperature increased. The sludge settleability was poorest at 40°C, improving at lower and higher temperatures. The population of microbes consisted of bacteria, protozoa and metazoa at temperatures from 20 to 40°C, while at 50°C, the microbial population consisted of bacteria and filamentous organisms only. The absence of protozoa and metazoa at 50°C was thought to reflect a change in microbial population from mesophiles to thermophiles. The decreased removal efficiencies were probably due to a decrease in microbial species, a lower MLSS level, and a lower oxygen transfer rate.

Earlier work adds support to these observations in the operation of an aerated lagoon in the treatment of kraft mill effluents at high temperatures (Lee *et al.*, 1978). BOD<sub>5</sub> and toxicity were removed satisfactorily up to 50°C. In particular, above 50°C, LC<sub>50</sub> toxicity to rainbow trout fingerlings was evident, whereas at lower temperatures, the effluent was non-toxic. Toxicity in pulp mill effluents is largely due to resin and fatty acids (Leach *et al.*, 1977). Thus,

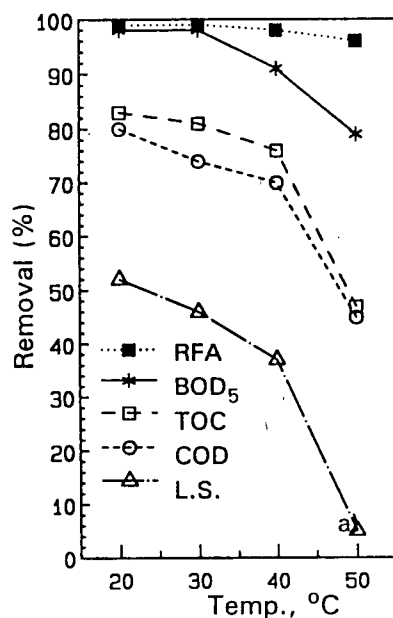


Figure 13. Contaminant removal efficiencies for RFAs, BOD<sub>5</sub>, TOC, COD, and lignosulfonates at varying temperatures (taken from Lo *et al.*, 1991).

at 50°C and below, the non-toxic effluent indicated a significant removal of resin and fatty acids.

From these research results, similar results are expected from an aerobic system such as the bioreactor of the whitewater membrane bioreactor when the temperature is increased. The removal of resin and fatty acids would probably become less efficient at around 50°C and the removal of other measured parameters such as TOC and COD may decrease at temperatures higher than 40°C.

## 2.5. Sequencing Batch Reactor

The choice of using sequencing batch reactors to investigate the bioreactor aspect of the whitewater membrane bioreactor was made because of its ease in construction and maintenance and its flexibility in control and operation. The particulars of the treatment cycle

can be easily adjusted to suit the treatment. The automation of a simple fill and draw operation is much less complex than that of a continuous flow system (CFS). A clarifier is not needed because of the built-in settling stage of the treatment cycle. In addition, the removal of compounds can be monitored over the react cycle to determine removals of more resilient materials after easily degradable material is removed.

Sequencing batch reactors are an extension of the simple draw/fill reactor design. The five process stages of fill, react, settle, draw, and idle repeat, allow a continuous treatment. Sequencing batch reactors (SBRs), used most extensively in municipal applications, differ from continuous flow systems (CFSs) in that the SBRs operate in a time sequence while CFSs operate in a space sequence. In other words, CFSs perform different operations in different tanks in sequence and are limited by their volume. SBRs, on the other hand, use timed sequences in the same location for the treatments such as reaction, aeration, and settling. Since time is much more easily manipulated than volume available for use, SBRs are much more flexible and simple in their treatment method than CFSs (Irvine and Ketchum, 1989).

#### **2.5.1. Sequencing Batch Reactor Treatment of High-Strength Wastes**

Since the whitewater treated in this study was expected to contain high concentrations of organics, investigating other applications of SBR systems in treating high-strength wastes is useful. SBR systems have been used successfully to treat a variety of high-strength wastes in investigative and operational situations ranging from agricultural applications at piggeries, slaughterhouses, and milking centres to industrial applications at palm oil refineries, petrochemical processing plants, and soybean fermentation plants to municipal applications at landfills and sewage treatment plants.



In order to provide an indication of typical SBR operating conditions and treatment quality, Table 6 provides details for treatment of landfill leachate (Ying *et al.*, 1986), milking centre waste (Lo *et al.*, 1988), and slaughterhouse waste (Hadjinicolaou, 1989).

These examples are a few of many examples of high-strength waste treatment by SBR systems. Examples from the pulp and paper industry, however, are few because CFS technology was preferred over SBR systems due to the volumes of waste treated and to the intensive labour required for the SBR systems before automation technology was developed.

Table 6. Operating conditions and treatment quality for SBR treatment of landfill leachate (Ying *et al.*, 1986), milking centre waste (Lo *et al.*, 1988), and slaughterhouse waste (Hadjinicolaou, 1989). nm = not measured, nr = not reported.

	Leachate	Milking Ctr.	Slaughterhouse
HRT [d]	2	0.83	3
SRT [d]	15.7	16.7	15
Reactor Vol [L]	500	5	137.5
Feed per cycle [L]	250	1.5	45.8
Cycle time [h]	24	6	24
React time [h]	10	3.5	21
Settle [h]	2	1.5	2.5
MLSS [mg/L]	10000	nr	3335
COD Inf [mg/L O <sub>2</sub> ]	5300	919	3512
COD Eff	1700	155	128
COD Removal [%]	68	83	96
TOC Inf [mg/L C]	2000	nm	nm
TOC Eff	536	nm	nm
TOC Removal [%]	73	nm	nm
BOD <sub>5</sub> Inf [mg/L O <sub>2</sub> ]	nm	270	1445
BOD <sub>5</sub> Eff	nm	13	14
BOD <sub>5</sub> Removal [%]	nm	95	99
Growth Yield [mg/mg TOC rem]	0.87	nr	nr

### **3. RESEARCH OBJECTIVES**

The overall goal of this research was to assess the feasibility of the biological stage of a biological membrane reactor system in the treatment of a simulated whitewater for an integrated mechanical newsprint mill. This research contributes to the assessment of this closure strategy in a mill application, with the ultimate goal being an effluent-free mill system. After consulting with PAPRICAN and examining the relevant available literature, the following research objectives were determined:

- (1) To investigate the operational viability at varying temperatures of the biological stage of a biological membrane reactor system as represented by an aerobic sequencing batch reactor, in the treatment of a simulated whitewater for an integrated mechanical newsprint mill.
- (2) To investigate the removal of conventional whitewater contaminants in an SBR operating at varying temperatures.
- (3) To investigate the removal of resin and fatty acids from whitewater in an SBR operating at varying temperatures.
- (4) To investigate the possible fates of the resin and fatty acids throughout the experimental period.

## 4.0. MATERIALS AND EXPERIMENTAL METHODS

### 4.1. Reactor

The reactor used was a 17 L acrylic cylinder, 59.7 cm in height and 19.1 cm internal diameter. Plastic and tygon 1.27 cm (1/2") internal diameter (ID) tubing was used for the effluent and influent lines and 0.95 cm (3/8") ID tubing was used for the nutrient lines (Figure 14). The effluent line was adjusted to a position corresponding to the volume of the effluent to be removed (approximately 5 L). Solids were wasted through the effluent line when the reactor was fully mixed. The reactor was aerated using a CSA Maxima aquarium aerator delivering an unimpaired flow of 5400 mL/min to a disperser made from 1.27 cm (1/2") ID rigid plastic gas tubing with pin holes in it at the bottom of the reactor. The aeration also served to mix the biomass. Automation of the sequencing batch reactor cycle of draw, fill and settle was achieved with a ChronTrol controller.

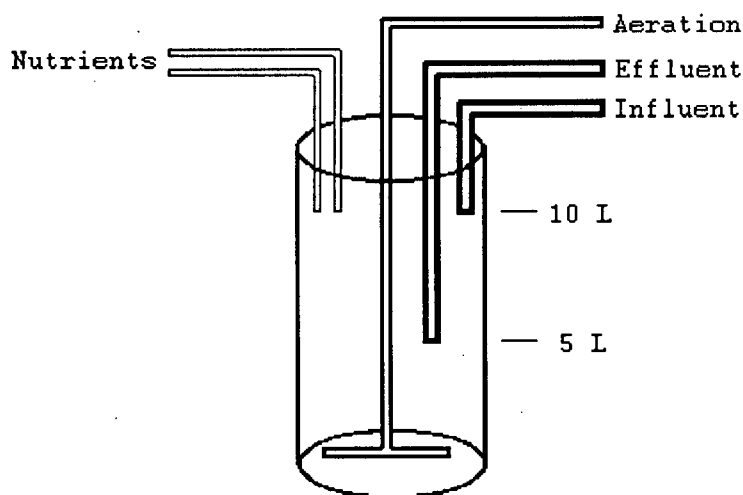


Figure 14. The set-up of the reactor with the influent, nutrients and aeration lines and the effluent line.

#### **4.1.1. Water Bath for Temperature Control**

The temperatures settings of 30, 40, 45 and 50°C were maintained by immersion of the SBR in a water bath. The water bath container was a polystyrene box, open at the top, with a bottom of 60 by 60 cm, and a height of 80 cm. Polystyrene foam board was used to line the inside and outside of the water bath and the exposed water surfaces, to minimize heat loss and to act as a partial barrier to minimize evaporation. The water bath was heated with a Haake D1 heater. The reactor was immersed in the bath up to the 9 L level to maintain the temperature needed. The water level in the bath was maintained manually, by replacing evaporated water with tap water as needed.

#### **4.1.2. Synthetic Whitewater Feed**

Since whitewater typical of closed mills is not obtainable presently, a whitewater was synthesized using TMP screw press pressate and evaporator bottoms obtained from a closed-cycle CTMP mill. Before preparing the synthetic whitewater, the pressate was settled for one hour to remove large particles and fibres without removing colloidal materials. Settled and unsettled pressate and evaporator bottoms were stored in carboys in a refrigerator at 4°C. To make the synthetic whitewater, the pressate was diluted one part in five with tap water to resin and fatty acid concentrations of about 15 to 20 mg/L. CTMP mill evaporator bottoms (35 mL, TDS =  $4 \times 10^5$  mg/L) were then added to the diluted pressate (5L) to achieve total dissolved solids (TDS) concentrations between 3000 and 4000 mg/L. At the beginning of the acclimatization period of the reactor, only diluted pressate without evaporator bottoms was fed to the reactor. Near the end of the acclimatization period (after Sept 13, 1993) and during the experimental period, the complete synthetic whitewater was used as influent.

The change in quality of the stored screw pressate was determined by sampling its resin and fatty acids content on most SBR sampling days. The results will be discussed in the Results and Discussion section (Chapter 5.). The COD and TOC of the screw pressate was not

monitored regularly because previous studies had indicated minimal degradation during storage (Elefsiniotis, 1994).

#### **4.1.3 Reactor Operation**

The biological reactor was operated as a sequencing batch reactor with an HRT of 48 hours. The reactor was operated at an SRT between 15 and 25 days. Just before the settling stage, while the reactor was fully mixed, a volume between 0 and 0.5 L of mixed liquor was wasted. Every 24 hours, aeration was stopped, allowing the reactor to settle for one hour. After settling, a volume of supernatant, adjusted for the volume of mixed liquor previously wasted, was pumped out of the reactor as treated effluent to make a total volume of 5 L exiting the reactor. Over a time period of 15 minutes, 5 L of influent was then pumped from a 25 L storage bucket, through a stainless steel tubing coil immersed in the water bath, into the reactor. The influent was pumped from the storage bucket through the heating coil to increase the influent temperature to minimize temperature shocks to the biomass. During the experimental runs at 20 and 30°C, the heating coil was not used. After the draw/fill cycle was completed, aeration was started again, mixing the biomass.

During the influent addition, 5 mL of  $\text{NH}_4\text{Cl}$  at a concentration of 0.103 gN/mL and 5 mL of  $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$  at a concentration of 0.1452 gP/mL were pumped directly into the reactor using Masterflex Tygon size 13 tubing over a period of 40 seconds. These nutrient additions were deemed necessary because the influent had very low nutrient levels (ortho-P: 0.8 mg P/L, NOx: 0.3 mg N/L,  $\text{NH}_3$ : 0.5 mg N/L). The concentrations of added nutrients were chosen by measuring the nutrient level at the end of a cycle to ensure that the added nutrients were still present at a sufficient level (about 5 mg/L of ortho-P and NOx as P or N).

Premixed reactor influent was kept at room temperature and fed to the reactor over a maximum period of 4 days. Since the influent was nutrient deficient, the separate addition of

nutrients directly to the reactor helped minimize biological growth in the influent storage bucket.

#### **4.1.4 Seed Organisms**

Organisms used to seed the reactor were obtained from a pulp and paper mill wastewater treatment system and a municipal treatment system. A sample of 2 L of mixed liquor from the wastewater treatment system of a paperboard paper mill was taken on July 12, 1993 and stored in a refrigerator overnight at 4°C. This seed was used to start the reactor on July 13, 1993, adding 8 L of diluted pressate as feed. The next day, the sequencing batch reactor cycle was started as described previously (section 4.1.3) and nutrients were added in excess of the requirements determined later. Over the next 6 days, the settled sludge decreased to a volume of about 800 mL and an MLVSS level of 700 mg/L (July 21, 1993).

Additional mixed liquor was added to increase the solids levels. A sample of 6.5 L of mixed liquor was taken from the activated sludge section of the UBC Civil Engineering municipal waste pilot plant on July 22, 1993 (MLSS = 3000 mg/L). After that day's settling and effluent draw, the municipal sludge was added and mixed with the reactor contents, making a total reactor volume of 11.5 L. The reactor contents were then settled for one hour and effluent was drawn off, reducing the reactor level to 8 L. Diluted pressate was added to fill the reactor to 10 L and aeration was started, resuming the normal reactor cycle. Addition of the municipal mixed liquor increased the MLVSS levels to 3550 mg/L.

#### **4.1.5 Biomass Acclimatization**

The organism population was allowed to grow and acclimatize to the waste and to the reactor conditions before experimenting began. A volume of 1 L of mixed liquor was wasted each day from July 29, 1993 until August 14, 1993 to assure that the initial seed organisms had

been replaced by new organisms. Then the wasting line was turned off to allow the reactor solids to increase.

The reactor volatile suspended solids (VSS) on August 19, 1993 was 1120 mg/L and after growing for two months, on October 26, 1993, the MLVSS was 5110 mg/L. To provide solids for another reactor, the reactor's solids were then divided on November 2, 1993, leaving the MLVSS levels at 3820 mg/L on November 4, 1993. The solids recovered to 5850 mg/L by November 12, 1993, when the experimental period began (day 0 of the experimental phase of reactor operation).

#### **4.2. Experimental Design**

The effect of SBR treatment on the quality of the whitewater was studied using the bench-scale SBR. Priority contaminants investigated were resin and fatty acids. Effective SBR operation and compound removal was monitored over the cycle of the SBR to determine when the effluent was free of contaminants. The removal efficiency of the reactor at higher temperatures was explored with emphasis on resin and fatty acids. The experimental period of the reactor ran from November 12, 1993 (day 0) to September 30, 1994 (day 322).

##### **4.2.1. Reactor Operating Parameters**

The operation of the reactor was governed by temperature and the maintenance of a viable biomass at an SRT higher than 15 days.

###### **4.2.1.1. Temperature**

The reactor was operated at five temperature settings: room temperature (between 16 and 22°C), 30, 40, 45 and 50°C (Table 7, Figure 15).



Table 7. Duration of temperature settings during the experimental period. SS = Steady State.  
T = Transition.

Temperature	Start Day	End Day	Length
20°C (SS)	0	74	74 days
20 - 30°C (T)	74	74	0 days
30°C (SS)	74	146	72 days
30 - 40°C (T)	146	152	6 days
40°C (SS)	152	217	65 days
40-45°C (T)	217	223	6 days
45°C (SS)	223	263	40 days
45-50°C (T)	263	272	9 days
50°C (SS)	272	322	50 days

For convenience, room temperature was assumed to average 20°C, though in reality, it ranged from 16 to 22°C, varying with outdoor weather. The temperature change from 20 to 30°C was made by imposing a single 10°C temperature increase. All other temperature transitions were effected by raising the temperature in steps over a period of 6 to 9 days (Table 8). Due to a power failure on July 24, 1994 or day 254, reactor temperature decreased below the 45°C setpoint for 7 hours.

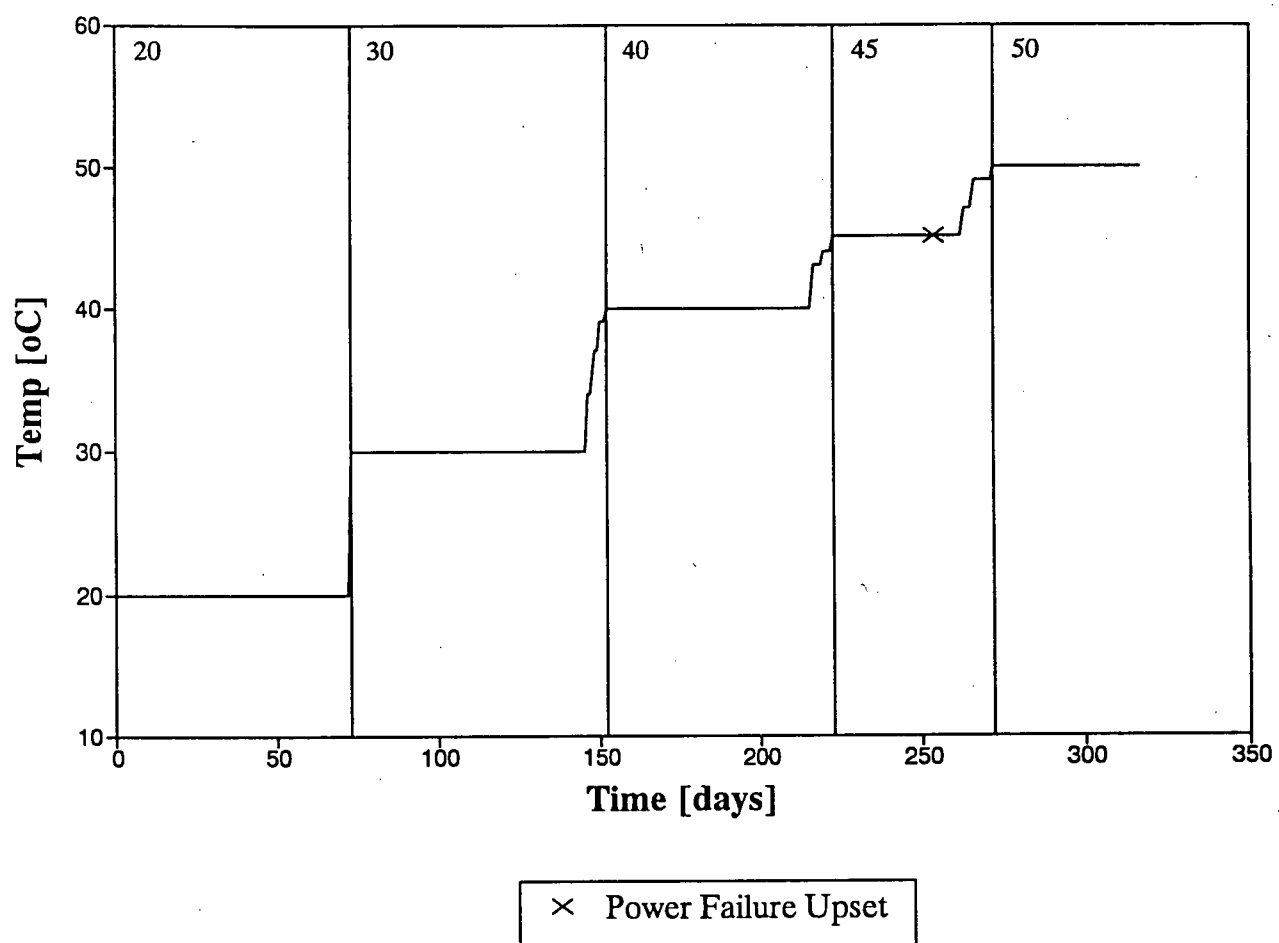


Figure 15. Temperature of reactor over experimental period.

Table 8. Temperature increments during the temperature transition periods.

Temperature Increment [°C]	Day	Temperature Increment [°C]	Day
20 to 30	73	40 to 43	217
30 to 34	146	43 to 44	220
		44 to 45	223
34 to 37	148	45 to 47	263
37 to 39	150	47 to 49	266
39 to 40	152	49 to 50	272

#### 4.2.1.2. Solids Retention Time

The operation of the reactor was intended to maintain a viable biomass at an SRT higher than 15 days. The SRT was calculated using the total VSS in the reactor divided by the total solids lost that day in the effluent and from wasting. These values were plotted using a 10-day moving average to smooth the data (Figure 16).

The system SRT was generally maintained between 15 and 25 days except during the 50°C run. SRT values decreased after the preceding temperature transition due to solids losses in the effluent because of poor settling, but the SRT recovered soon after. The control parameter shifted from SRT control to maintenance of MLVSS concentration at 50°C, when wasting was terminated. Thus at 50°C, despite the low MLVSS levels maintained, the elimination of solids wasting resulted in an SRT of about 30 days.

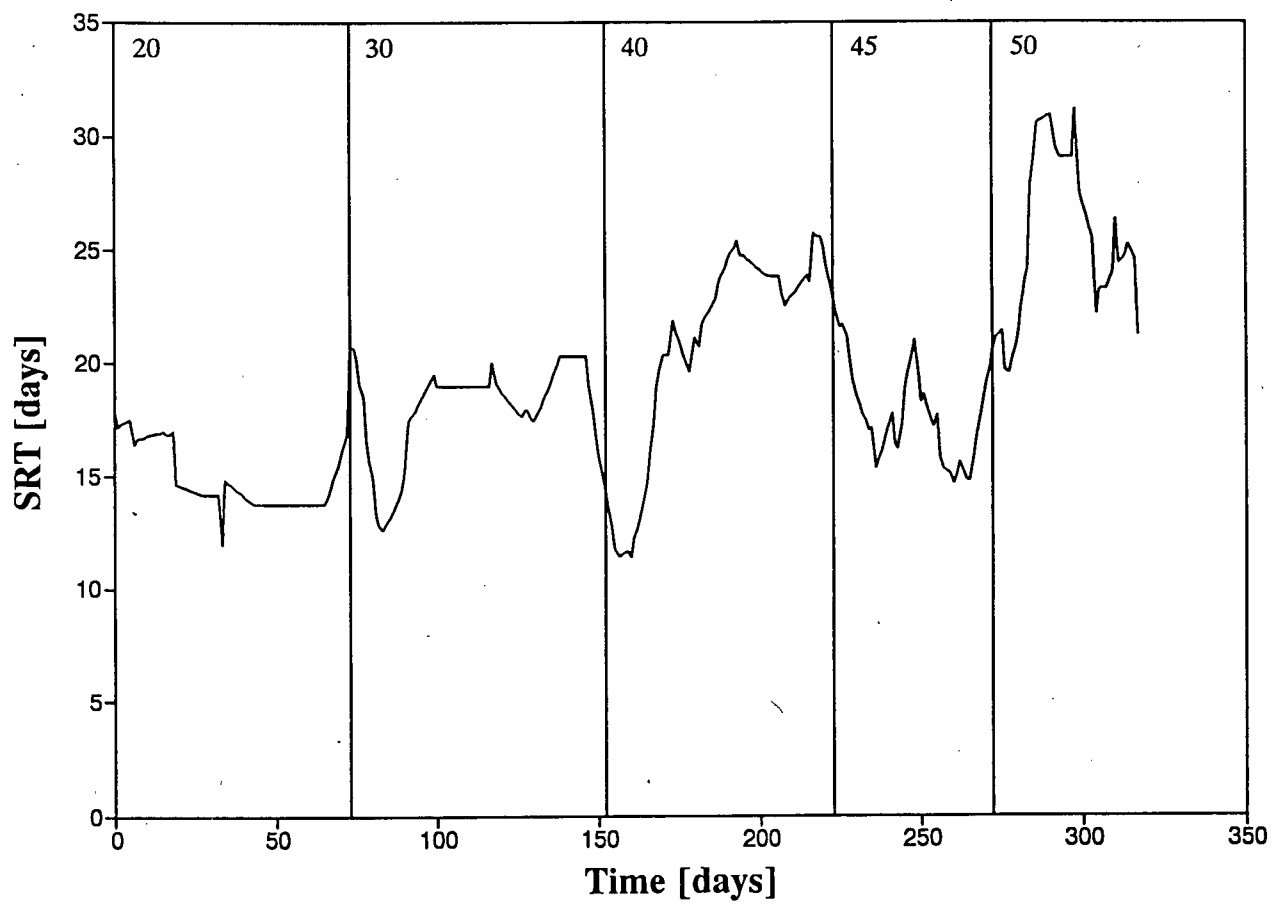


Figure 16. SRT versus time using a 10-day moving average during experimental period.

#### **4.2.2. Sampling**

The reactor was operated at each steady state experimental condition for as long as it took to sample and process four or five sets of samples, usually from 40 to 74 days. On a sampling day, the reactor was sampled for resin and fatty acids, TOC, COD and VSS (Table 9). Influent samples were taken from the influent storage bucket at room temperature, the contents of which were mixed thoroughly before sampling. Effluent samples were taken in a similar fashion from a bucket where the effluent had collected. Samples of influent and effluent were analyzed for VSS, TDS, COD, TOC and resin and fatty acids.

Reactor contents were sampled for MLVSS and resin and fatty acids at 22.5 hours, near the end of the previous day's SBR cycle, just prior to settling. In addition, resin and fatty acid samples were taken at zero hour, at the cycle's beginning, just after the draw/fill sequence and at the start of aeration, and at 1, 2, 4, 6, 9, 12, 18 and 22.5 hours during the reactor's aerating stage (Table 9).

#### **4.2.3. Sample Preservation and Storage**

Samples were stored at 4°C in a refrigerator for various analyses. Samples for resin and fatty acids were stored for less than 7 days at pH 9. The alkaline pH was achieved by adding drops of 0.1 N and/or 1 N NaOH. COD and TOC samples were stored in the refrigerator for up to 28 days at less than pH 2. The acidity was achieved by adding drops of 10% and/or 100% H<sub>2</sub>SO<sub>4</sub>. Samples for nutrients were stored at 4°C and were analyzed within 4 hours of sampling. Samples for VSS and TDS were stored at 4°C and were analyzed the day of the sampling.

Table 9. The timing of the cycle activity and the samples taken. ML = Mixed liquor. Inf = Influent. Eff = Effluent. VSS = Volatile suspended solids. RFA = Resin and fatty acids.

Cycle Activity	Cycle Time [h]	Samples Taken
Aeration	22.5	ML VSS, RFA
Settling	22.5	
Effluent	23.5	Eff COD, TOC, VSS, RFA
Influent	23.7	Inf COD, TOC, VSS, RFA
Aeration	0	ML RFA
Aeration	1	ML RFA
Aeration	2	ML RFA
Aeration	4	ML RFA
Aeration	6	ML RFA
Aeration	9	ML RFA
Aeration	12	ML RFA
Aeration	18	ML RFA
Aeration	22.5	ML RFA
Settling	22.5	
Effluent	23.5	
Influent	23.7	

#### 4.2.4. Analytical Techniques and Equipment

##### 4.2.4.1. Resin and Fatty Acid Analysis

Resin and fatty acids were measured using a PAPRICAN in-house method adapted from the method proposed by De Boer and Backer (1954) and modified to an extraction pH of 9

according to Voss and Rapsomatiotis (1985). Since resin and fatty acid concentrations were high, a sample volume of 5 mL was extracted with two 5 mL volumes of methyl-t-butyl ether instead of the prescribed 50 mL of sample and total 100 mL of solvent. The resin and fatty acids were methylated after extraction using diazomethane gas carried by nitrogen gas. The methylated extracts were concentrated with nitrogen gas and then diluted to 1 mL using a solvent base of methyl-t-butyl ether and stored at -20°C until analyzed by gas chromatography. Methyl-t-butyl ether was used as a base solvent because less precipitation occurred during storage than with octane. The specific target compounds measured were fatty acids (palmitic, linoleic, linolenic, oleic, and stearic acids) and resin acids (pimaric, sandaracopimaric, isopimaric, palustric, levopimaric, dehydroabietic, abietic, and neoabietic acids) using methyl heneicosanoate and tricosanoic acid as internal standards for quantity and quality control (Source: Helix Biotech Corp., Richmond, B.C.). Palustric and levopimaric acids were reported as a sum of the two because separating the two compound peaks was difficult. DHA was used as a methylation standard and thus all resin and fatty acid values reported are in units of mg/L of DHA throughout this paper so the y-axes of graphs showing resin acids or fatty acids are comparable.

#### **4.2.4.2. Gas Chromatography**

Analysis of resin and fatty acids was carried out on two Hewlett Packard gas chromatographs, models 5880A and 5890 Series II, with flame ionization detectors and using a 30 m DB-1 fused silica column of 0.32 mm internal diameter and a 0.25 µm film thickness (J&W Scientific, Folsom, CA). The carrier gas used was helium at a linear velocity of 20 cm/s at 290°C. The FID makeup gas combined helium (20 mL/min), hydrogen (30 mL/min) and air (400 mL/min). The temperature program was improved upon until an efficient quick regime was found for the compounds investigated. The injection temperature was 275°C and the detector temperature was 290°C. The length of the run was 48.16 minutes and the temperature ramping is detailed in Table 10.

Table 10. The temperature program used in the detection of RFAs with the gas chromatograph.

Duration [min]	Temp [°C]	Temp change rate [°/min]
2.00	45	0
9.66	changing	15
1.00	190	0
25.00	changing	1
0.50	215	0
5.00	changing	15
5.00	290	0

#### 4.2.4.3. Total Organic Carbon Assays

Filtered samples were analyzed for total carbon and inorganic carbon, yielding total organic carbon values according to a standardized method using a Shimadzu AS1-502 automatic carbon analyzer (Greenberg *et al.*, 1985).

#### 4.2.4.4. Chemical Oxygen Demand

Chemical oxygen demand (COD) was measured for unfiltered and filtered samples using the closed reflux, colorimetric method (Greenberg *et al.*, 1985) with the Hach COD heater and a Bausch and Lomb Spectronic 88 spectrophotometer. COD analysis was performed without mercury because using mercury decreased values by only about 10%. In addition, using the method without mercury avoids the disposal expense of the hazardous waste produced in the COD analysis using mercury.



#### **4.2.4.5. Nutrients**

Ammonia, NO<sub>x</sub>, and ortho-P were measured in filtered samples using a Lachat QuikChem AE autoanalyzer (Greenberg *et al.*, 1985).

#### **4.2.4.6. Suspended Solids**

Suspended solids were measured using a standardized method (Greenberg *et al.*, 1985). Total suspended solids (TSS), VSS and TDS were measured directly with the use of Whatman Glass Microfibre filters (5.5 cm diam., 934-AH) , evaporating dishes and a muffle furnace.

## **5. RESULTS AND DISCUSSION**

In this section, results describing the operation of the reactor are discussed. A description of the characteristics of the influent and its constituents illustrates the reactor feed. The behaviour of the reactor is described including the removal of conventional lumped parameter contaminants such as TDS, COD and TOC during the experimental phase. Since resin and fatty acids are considered by the pulp industry to be problem compounds, their behaviour in the reactor at different operating temperatures is reported.

### **5.1. Influent Characteristics**

The influent to the reactor was a mixture of TMP screw pressate and CTMP evaporator bottoms as discussed in section 4.1.2 of Materials and Methods. Several batches of screw pressate and evaporator bottoms were obtained throughout the experimental period to maintain the feed cycle of the reactor (Table 11). The feeding of the reactor from new batches of screw pressate and evaporator bottoms was started either immediately or soon after collection. A storage study was performed to determine the effect of storage on the characteristics of the pressate.

#### **5.1.1. Screw Pressate**

The periods of use of screw pressate in Table 11 sometimes overlap because while changing from an old batch to a new batch, mixtures of old and new pressate were used to ease the transition. Table 12 describes the mixtures used during transitions.

Table 11. The collection dates and period of use of the batches of screw pressate and evaporator bottoms during the acclimatization and experimental periods. ACC = Acclimatization period.

Screw Pressate			Evaporator Bottoms		
Batch	Collection	Period of Use	Batch	Collection	Period of Use
1	June 28, 1993	ACC, 0 - 12	1	Aug 10, 1993	ACC, 0 - 130
2	Nov 25, 1993	13 - 167	2	Mar 14, 1994	131-284
3	Apr 12, 1994	161 - 317	3	July 27, 1994	285-322
4	July 18, 1994	259 - 322			

Table 12. The mixture proportions used during transitions from old to new feed batches.

Transition	Day	Mixture	
		Old	New
From Batch 2 to 3	161	50%	50%
	166	25%	75%
	168	0%	100%
From Batch 3 to 4	259	75%	25%
	285	50%	50%
	310	25%	75%
	318	0%	100%

#### 5.1.1.1. Screw Pressate Storage Study

Since batches of screw pressate were required to be stored for long periods of time, they were monitored periodically to check for consistency. The important contribution of the screw pressate to the synthetic influent was resin and fatty acids, so the resin and fatty acid levels were monitored throughout the experimental period (Figures 17, 18, and 19). Resin and fatty acids, according to the analysis method used (Section 4.2.4.1.), are reported in units of mg DHA/L throughout this paper so the y-axes of graphs showing resin acids or fatty acids are comparable. The resin and fatty acid characteristics of the screw pressate in the batches 2, 3 and 4 that were used during the experimental period are summarized in Table 13.

In the second batch, the RFA, RA and FA appeared to decrease over time, but this trend is inferred from only four sample points (Figures 17, 18 and 19). A possible explanation for the two lower sample points in the latter part of the storage period of the second batch is a possible lower recovery in the analysis, which would yield proportionately lower numbers for all resin and fatty acids. Unfortunately, the quality assurance and quality control (QA/QC) data for these points are not available so this possible explanation cannot be confirmed.

Within the screw pressate batches 3 and 4, the total resin and fatty acids did not decrease over storage. As well, the individual resin and fatty acid concentrations in the third and fourth batches did not decrease.

Other variables such as TOC, total chemical oxygen demand (TCOD) and DCOD were not monitored regularly because, in a parallel study, Elefsiniotis (1994) found little degradation of these organics in batches 2 and 3 of screw pressate. TDS was not monitored regularly because the TDS contribution of screw pressate to the feed was small compared to the contribution from the evaporator bottoms. VSS was not monitored regularly because biological growth was not expected to occur under the storage conditions used.

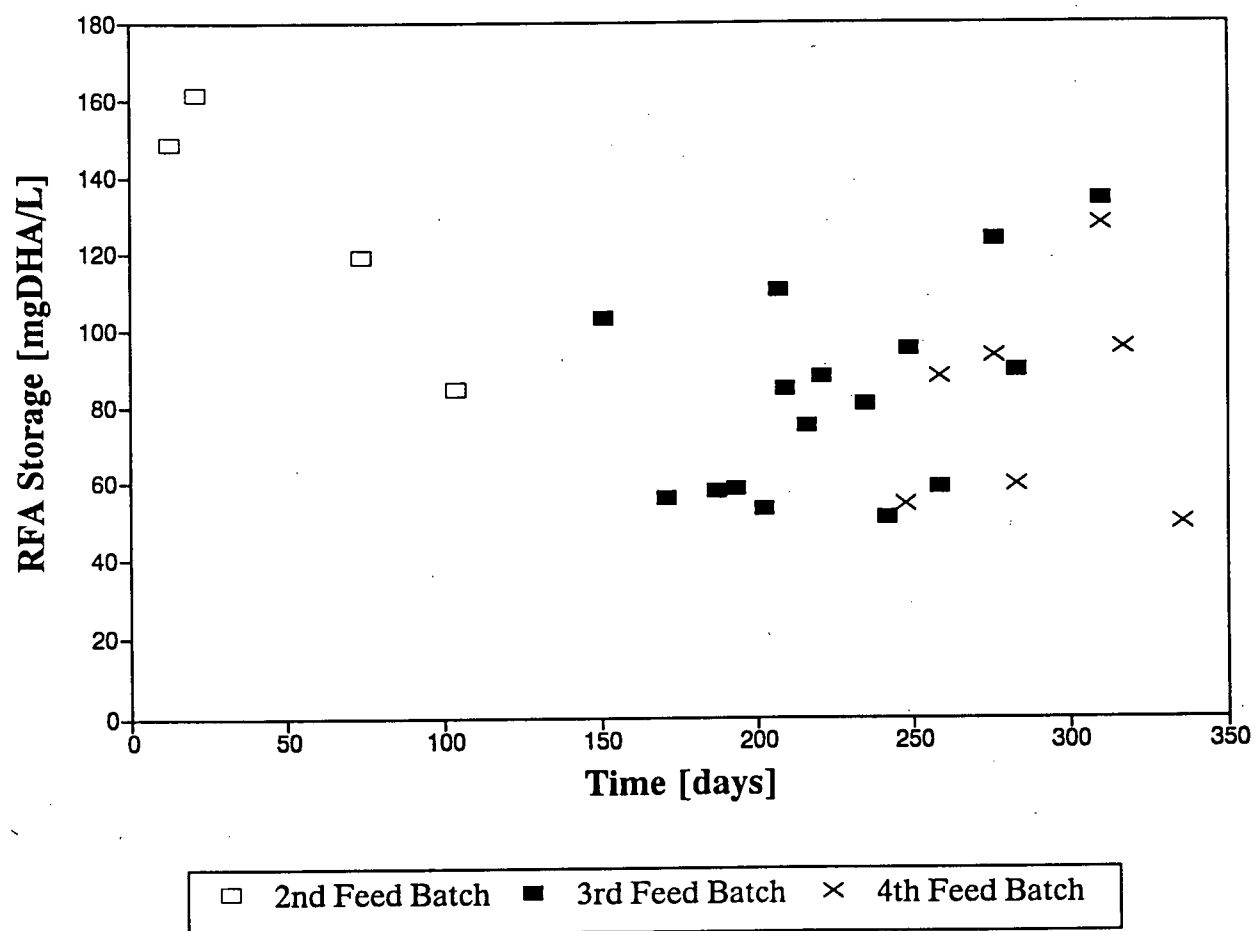


Figure 17. The total resin and fatty acid concentrations of screw pressate in storage. Batch 2 and the first three points in batch 3 were monitored by Elefsiniotis (1994).

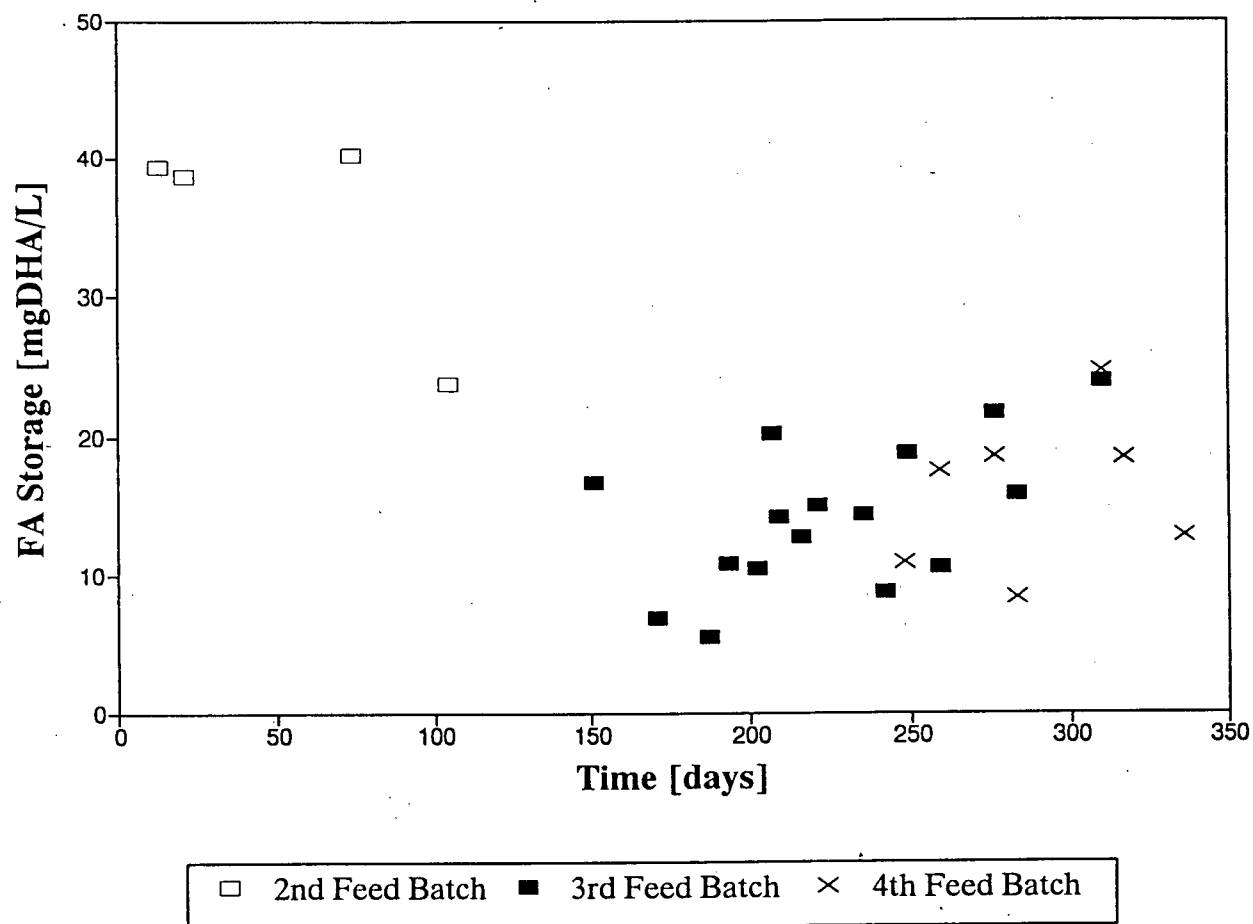


Figure 18. The total fatty acid concentrations of screw pressate in storage. Batch 2 and the first three points in batch 3 were monitored by Elefsiniotis (1994).

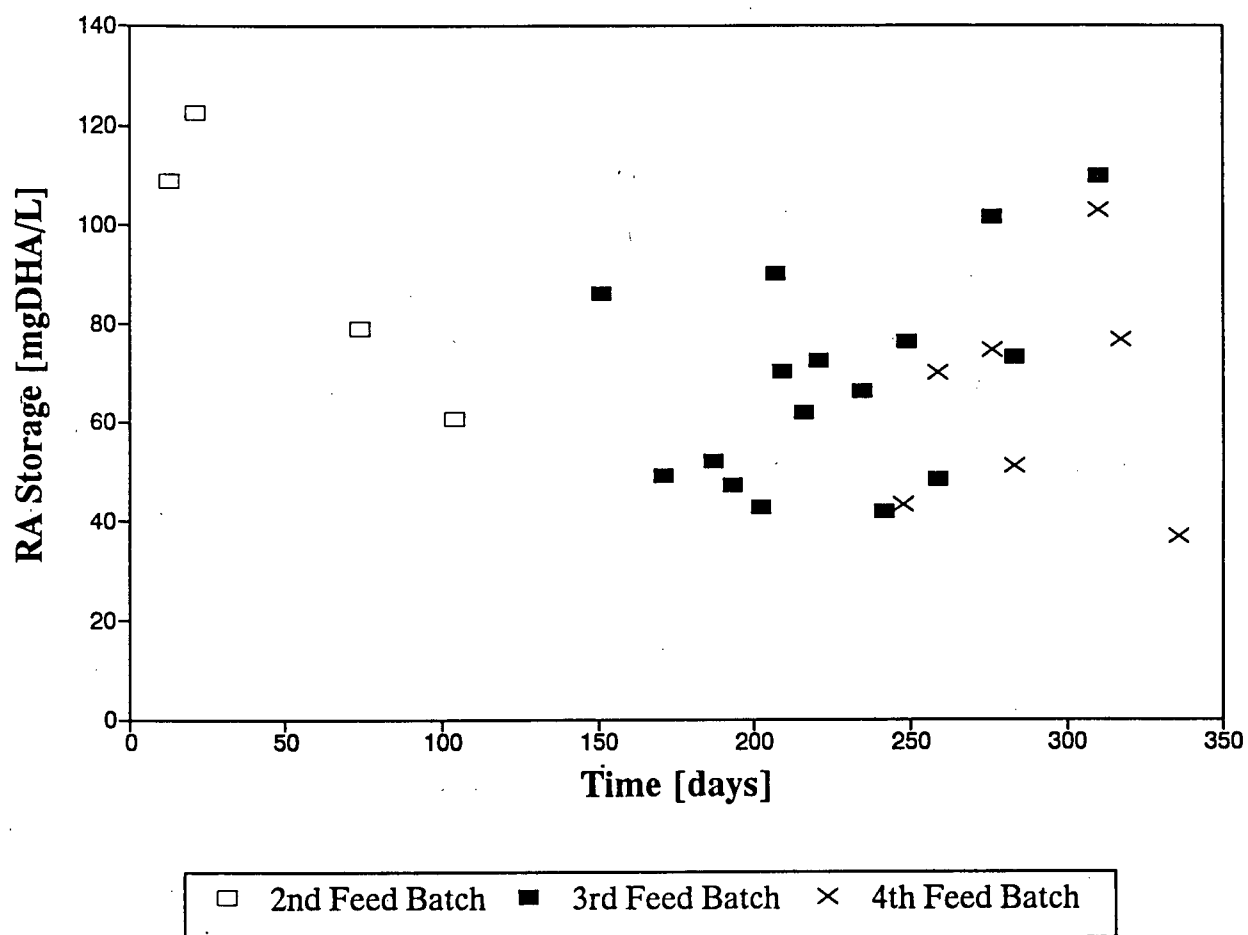


Figure 19. The total resin acid concentrations of screw pressate in storage. Batch 2 and the first three points in batch 3 were monitored by Elefsiniotis (1994).

Table 13. The resin and fatty acid screw pressate characteristics. FA = Total fatty acids. RA = Total resin acids. RFA = Total resin and fatty acids. SD = Standard deviation. Batch 2 and part of Batch 3 were monitored by Elefsiniotis (1994).

Batch	Component	Minimum [mg/L]	Maximum [mg/L]	Average [mg/L]	SD [mg/L]
2	FA	23.8	40.2	35.5	6.8
	RA	60.7	109.1	92.8	24.4
	RFA	84.6	161.4	128.4	29.6
3	FA	5.5	24.0	14.2	5.3
	RA	41.9	101.5	68.2	21.0
	RFA	53.1	133.9	82.4	26.0
4	FA	8.4	24.8	16.0	5.2
	RA	36.7	102.9	65.0	21.2
	RFA	49.6	127.7	81.0	26.1
Overall	FA	5.5	40.2	17.9	9.3
	RA	36.7	109.1	71.1	23.6
	RFA	49.6	161.4	89.1	31.4

Pressate from the second batch was sampled for analysis on August 5, 1993. The TDS and VSS results are shown in Table 14. The influent values show the contribution of various parameters of the screw pressate to the influent. The other batches of screw pressate were not sampled for solids because the synthetic influent itself was monitored throughout the experimental period.



Table 14. The TDS, TSS and VSS results from the analysis of an August 5, 1993 sample of the second batch of screw pressate and their contributions to the final influent.

TDS [mg/L]	Inf TDS [mg/L]	VSS [mg/L]	Inf VSS [mg/L]
3173	635	434	87
		492	98

The characterization of the TDS and VSS in the screw pressate (Table 14) provided useful information for the determination of the amount of evaporator bottoms to be added to achieve final influent TDS concentrations of between 3000 and 4000 mg/L. The screw pressate contribution of VSS to the influent was minimal. Most of the VSS in the screw pressate was expected to be non-viable organic matter such as wood material because the process by which the screw pressate are produced is not conducive to the survival of organisms.

The fourth batch of screw pressate was measured for TCOD and TOC on July 18, 1994. TCOD was found to be 4320 mg/L and TOC was measured at 1075 mg/L, values comparable to Elefsiniotis' study (1994) of the first and second batches of screw pressate. Therefore, the contribution of the screw pressate to the TCOD and TOC of the influent was consistent throughout the experimental period.

#### 5.1.2. Evaporator Bottoms

Evaporator bottoms, the other constituent of the synthetic influent, were not monitored regularly because their main contribution to the synthetic influent was TDS and that was monitored through regular monitoring of the influent for TDS. The first batch of evaporator

bottoms was analyzed for VSS, TDS and TOC and their contributions to the influent were calculated (Table 15).

Table 15. VSS, TDS and TOC levels of evaporator bottoms and their contributions to the final influent.

Date	VSS [mg/L]	Inf VSS [mg/L]	TDS [mg/L]	Inf TDS [mg/L]	TOC [mg/L C]	Inf TOC [mg/L]
Aug 23, 1993	9,600	67	215,000	1505		
	10,840	76	414,560	2902		
Aug 24, 1993					110,000	770
Oct 26, 1993			386,800	2708		

Table 15 shows that the contribution of VSS in the influent by evaporator bottoms is low. Most of the VSS in the evaporator bottoms was expected to be non-viable organic matter such as wood material because the process by which the evaporator bottoms are produced is not conducive to the survival of organisms. By adding the TDS components of the influent for the screw pressate (Table 14) and the evaporator bottoms (Table 15), the desired TDS level of between 3000 and 4000 mg/L was confirmed.

### 5.1.3. Influent

A diluted mixture of TMP screw pressate and CTMP evaporator bottoms made up the synthetic influent. The influent characteristics throughout the experimental period are summarized in Table 16 and detailed in graphs to follow.

Table 16. The maximum and minimum values, the average value and the standard deviation of the influent volatile suspended solids (VSS), total organic carbon (TOC), dissolved chemical oxygen demand (DCOD), total chemical oxygen demand (TCOD), and total resin and fatty acids (FA, RA, and RFA) throughout the experimental period.

Measurement	Units	Minimum	Maximum	Average	SD
VSS	[mg/L]	60	760	380	360
TDS	[mg/L]	2980	5160	3840	650
TOC	[mg/L C]	840	1360	1040	110
TCOD	[mg/L O <sub>2</sub> ]	2590	5530	3560	710
DCOD	[mg/L O <sub>2</sub> ]	2300	3190	2770	210
FA	[mg/L]	1.1	50.7	12.7	10.2
RA	[mg/L]	4.5	55.1	16.7	11.3
RFA	[mg/L]	6.6	105.8	29.3	21.1

Figure 20 shows the VSS concentrations of the influent throughout the experimental phase. Using the VSS measurements of the screw pressate and evaporator bottoms, the synthetic influent was expected to have a VSS concentration of about 100 mg/L due to volatile suspended material from the stored constituents. Fluctuations in VSS might have occurred due to the inclusion of organic material such as wood fines in the influent samples. After cleaning the influent bucket, the solids level was observed to drop, indicating that another factor in VSS fluctuations was VSS accumulation in the influent bucket due to organic matter settling to the bottom, adhering to the sides or floating at the surface. Although the influent bucket was cleaned routinely to minimize the impact of biological activity on influent

characteristics, some microbial growth may have occurred. A refrigerated storage facility for the influent would have reduced the possibility of biological growth.

A BOD<sub>5</sub> assay determined the oxygen demand of the influent sampled on September 28, 1993 (Table 17). TCOD was about twice the concentration of the BOD<sub>5</sub>.

Table 17. The BOD<sub>5</sub>, TOC and COD for the same influent sample on September 28, 1993.

BOD <sub>5</sub>	TOC	TCOD	DCOD
[mg/L O <sub>2</sub> ]	[mg/L C]	[mg/L O <sub>2</sub> ]	[mg/L O <sub>2</sub> ]
1252	735	2500	2150

## 5.2. Conventional Contaminants During Experimental Phase

Measurements describing the status of the reactor such as VSS are discussed. Conventional contaminants such as TDS, TOC and COD were monitored over the experimental phase and are reported.

### 5.2.1. Volatile Suspended Solids

To maintain adequate treatment, the reactor was operated so that sufficient solids concentrations were maintained at a target level of 5000 mg/L. The VSS concentrations in the effluent are plotted for the complete experimental period in Figure 21. Increased solids in the effluent due to poor settling were observed after all of the temperature changes, except that from 45 to 50°C. When the effluent VSS levels responded to a temperature change, the effluent solids returned to normal levels of less than 200 mg/L between 17 and 27 days after the first temperature increment of the temperature change.

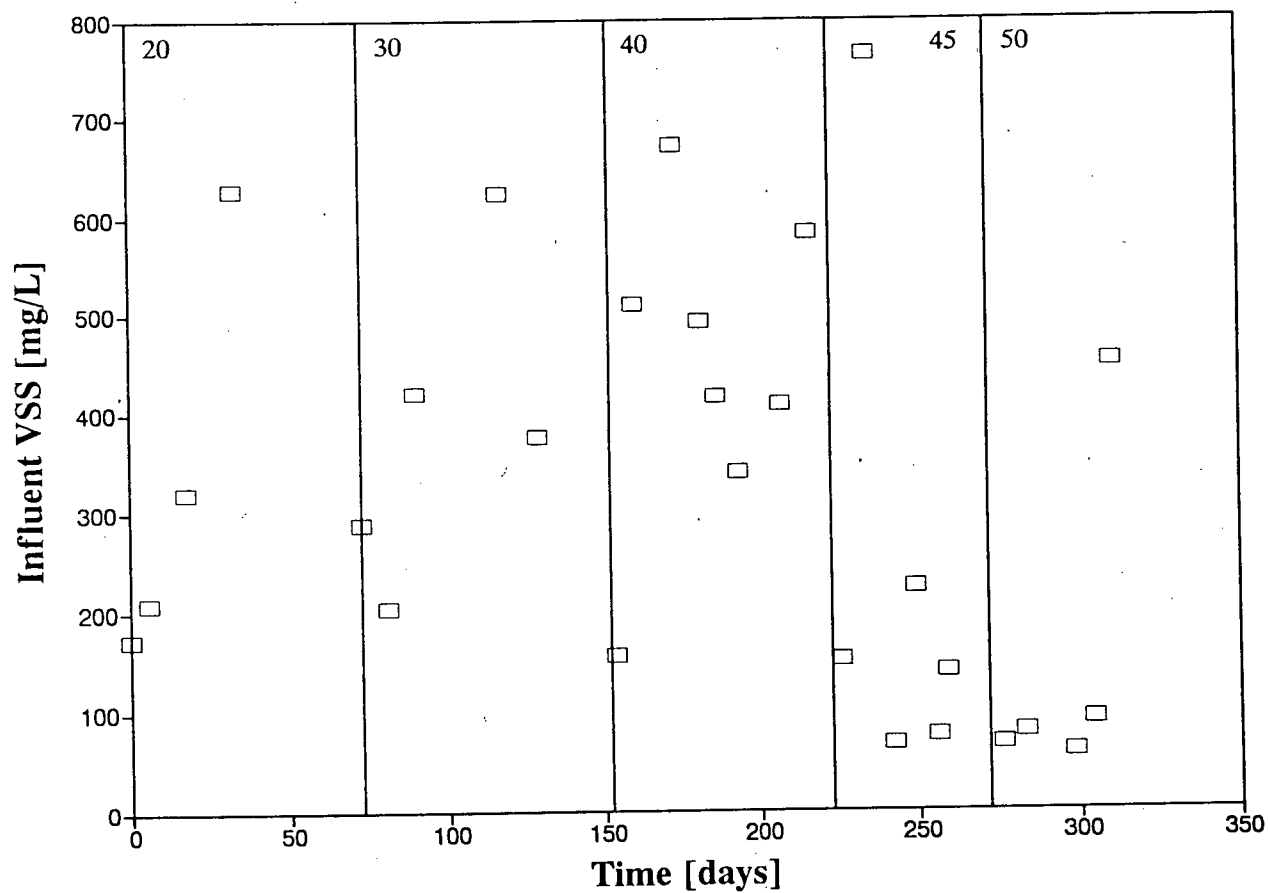


Figure 20. The VSS concentrations of the synthetic influent throughout the experimental period.

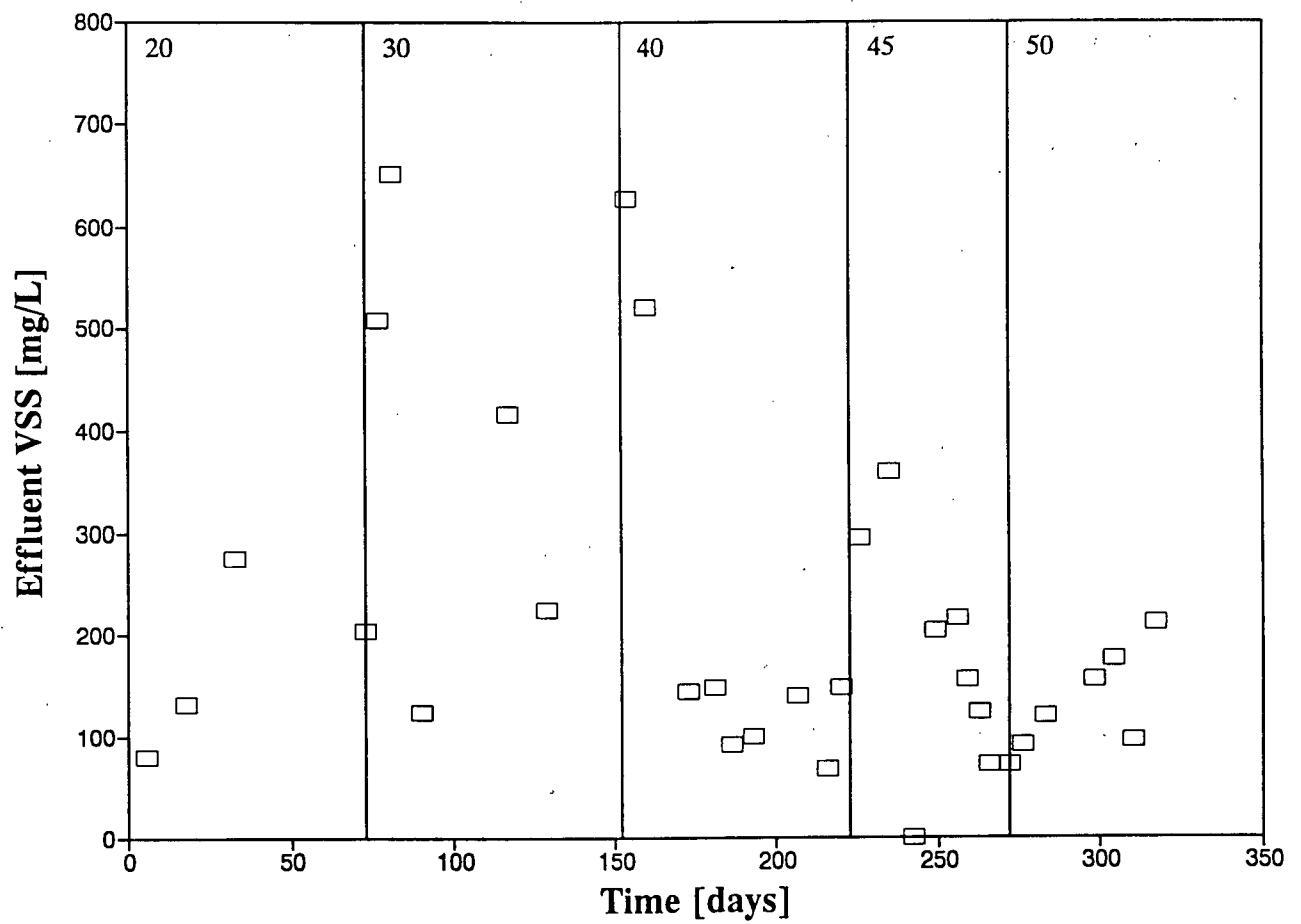


Figure 21. VSS concentrations in the effluent throughout the experimental period.

The mixed liquor VSS concentrations in the reactor are plotted for the complete experimental period in Figure 22. Wasting began on day 0 of the timeline and it took about 20 days for the reactor VSS concentration to reach steady state. The biomass concentrations in the reactor remained between 4000 and 6000 mg/L until the 45°C run, during which solids levels dropped dramatically. At 45°C, a power failure on day 254 resulted in a decrease in reactor temperature over a 7 hour period accompanied by a loss of aeration for 24 hours. This stress on the biomass combined with the stress of the recent temperature change were the probable causes of the decrease in biomass concentration. Poor settling during temperature changes resulted in additional VSS loss in the effluent (Figure 21). To stabilize the MLVSS content at about 2000 mg/L during the 50°C treatment, intentional wasting was terminated on day 281 and any solids wasted thereafter came from unintentional solids loss in the effluent. Thus, near the end of the experimental program, SRT control was relinquished in order to maintain reactor biomass levels.

The extent of biomass growth for different temperature runs was assessed using a mass balance approach. The net VSS production was calculated by subtracting the cumulative influent VSS from the sum of the cumulative effluent + wasted VSS and cumulative change in the reactor VSS.

$$\begin{array}{lcl} \text{Net} & \text{Growth} & \\ \text{or} & \text{or} & \\ \text{Decay} & \text{Decay} & \end{array} = \begin{array}{l} \text{Cum Effluent VSS} + \text{Cum Waste VSS} \\ + \text{Cum } \Delta \text{MLVSS} - \text{Cum Influent VSS} \end{array} \quad \text{Eqn. 1}$$

This calculation assumes that all of the influent VSS accumulated rather than degraded in the reactor. This assumption might underestimate the net solids produced if it is not completely valid.

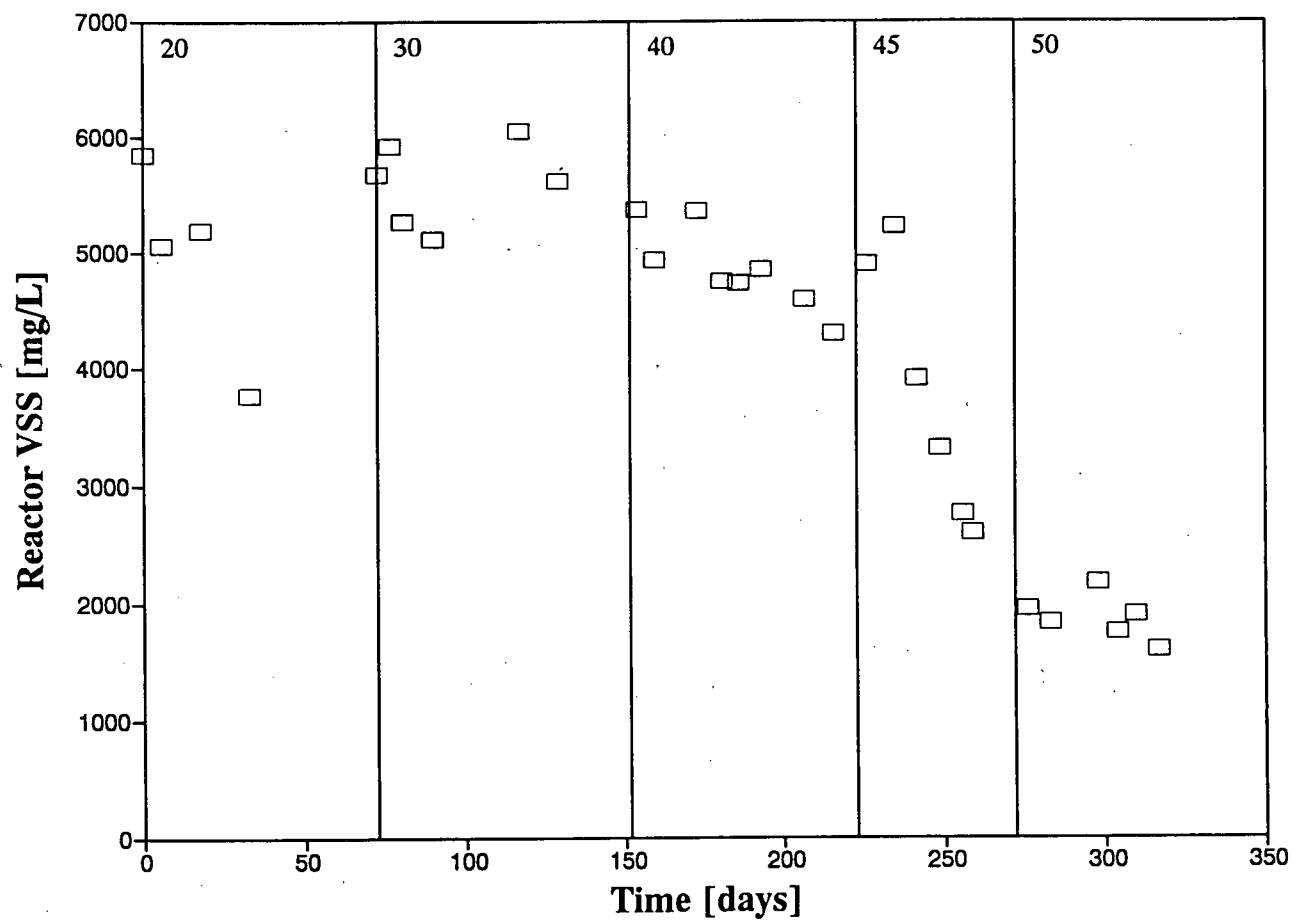


Figure 22. MLVSS concentrations in the reactor throughout the experimental period.



A cumulative VSS plot gives a visual representation of the net biomass growth and the relative importance of each input and output from the system. A plot of the cumulative effluent, influent and waste VSS and the reactor VSS, along with the net solids produced is shown in Figure 23. For this plot, the y-axis values at day  $n$  were determined by summing the daily VSS levels from day 0 to day  $n$  using VSS concentrations ( $X$ ) and daily flow rates ( $Q$ ) (Equations 2, 3, 4, and 5) and using Equation 1 to calculate the net VSS production up to day  $n$ . The concentration of VSS in the reactor during the experimental period is plotted on the graph to display the relative difference of the cumulative VSS values with the actual reactor VSS level.

$$\text{Cumulative Effluent VSS: } \sum_{t=0}^n Q_t^{\text{Eff}} \cdot X_t^{\text{Eff}} \quad \text{Eqn. 2}$$

$$\text{Cumulative Waste VSS: } \sum_{t=0}^n Q_t^{\text{Waste}} \cdot X_t^{\text{Reactor}} \quad \text{Eqn. 3}$$

$$\text{Cumulative Influent VSS: } \sum_{t=0}^n Q_t^{\text{Inf}} \cdot X_t^{\text{Inf}} \quad \text{Eqn. 4}$$

$$\begin{aligned} \text{Cumulative } \Delta \text{MLVSS: } & \sum_{t=0}^n V_r \cdot (X_t^{\text{Reactor}} - X_{t-1}^{\text{Reactor}}) \\ & = V_r \cdot (X_n - X_0) \quad \text{Eqn. 5} \end{aligned}$$

The cumulative  $\Delta \text{MLVSS}$  simplifies to the volume of the reactor ( $V_r=10\text{L}$ ) times the difference between the VSS concentration of the mixed liquor on day  $n$  ( $X_n$ ) and the initial mixed liquor VSS concentration ( $X_0$ ).

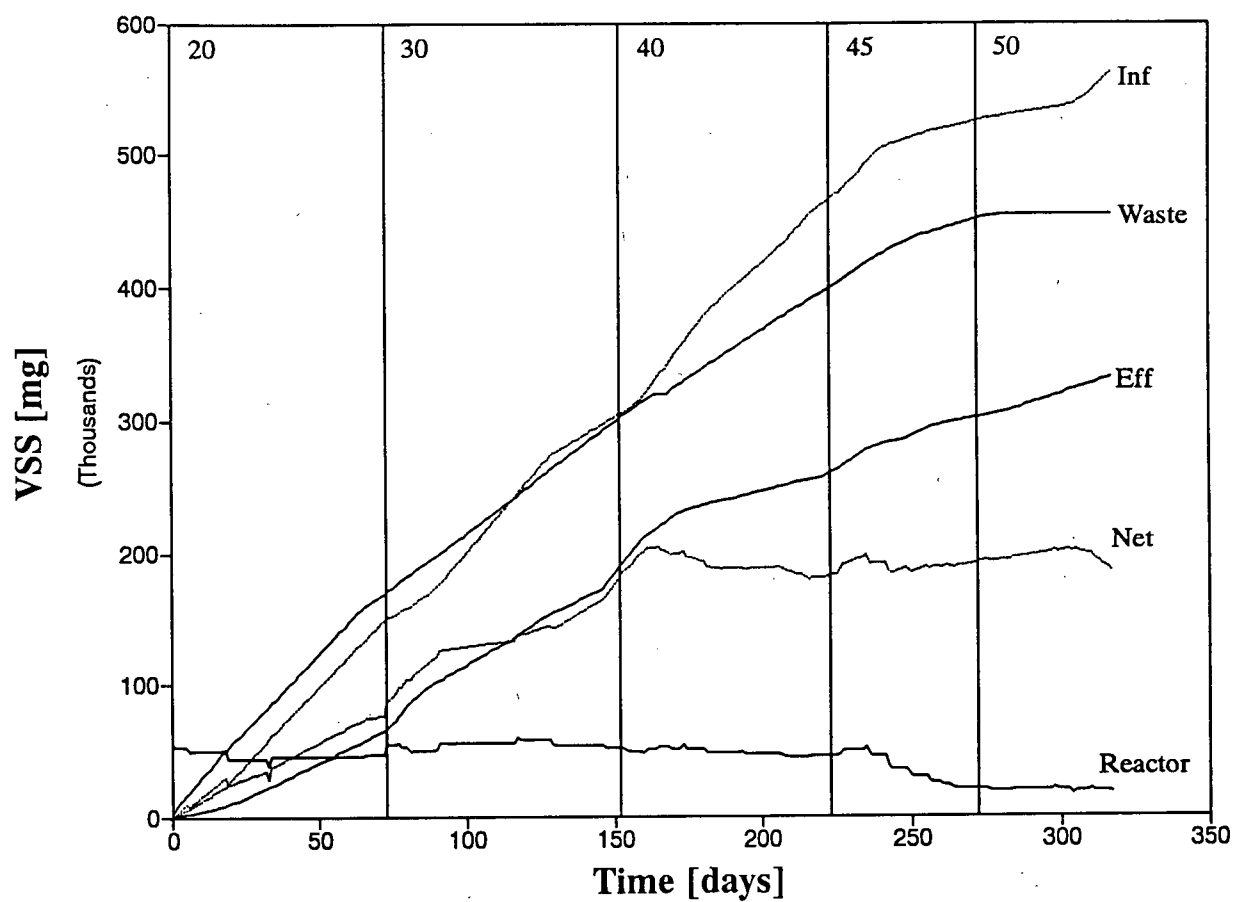


Figure 23. Cumulative VSS in the effluent, influent, waste sludge, and the reactor and the cumulative net VSS produced during the experimental period.

The cumulative net VSS production (Figure 23) increases during the 20 and 30°C runs, but levels off during the higher temperature runs, indicating little, or no biomass production at 40, 45 and 50°C. This interpretation relies on the validity of the assumption that all influent solids entering the reactor accumulate, rather than being biodegraded.

### **5.2.2. Removal of Organics During Experimental Phase**

The main aim in investigating the performance of the reactor was to assess the removal of problem compounds such as resin and fatty acids. An indicator of this was the change in conventional performance parameters such as TDS, TOC and COD through treatment. Throughout the experimental period, starting November 12, 1993, organics removal was measured through TDS, TOC and COD monitoring of the influent and effluent. Resin and fatty acids were also measured, but they are discussed later in section 5.4.

#### **5.2.2.1. Total Dissolved Solids**

In general, the TDS in the influent varied between 3000 and 4500 mg/L (Figure 24). The TDS in the effluent ranged from 2000 to 4500 mg/L. During the experimental runs at 20 and 30°C, the effluent TDS concentration was about 2000 mg/L. During the 30 to 40°C transition, the effluent TDS levels were equivalent to those of the influent. During the 40°C run and during the 40 to 45°C transitions, the TDS in the effluent stabilized at about 2500 mg/L. Soon after the temperature change to 45°C, the TDS content of the effluent was similar to that of the influent for the remainder of the 45°C and the 50°C runs.

The removal efficiency of TDS (Figure 25) was about 40% during the 20, 30 and 40°C runs, except during temperature transitions when there was no removal. Removal efficiencies decreased during the 45°C run, fluctuating around zero for the remainder of the 45°C and the 50°C runs. Figure 26 summarizes the average influent and effluent concentrations and the removal efficiencies for the different temperature runs.

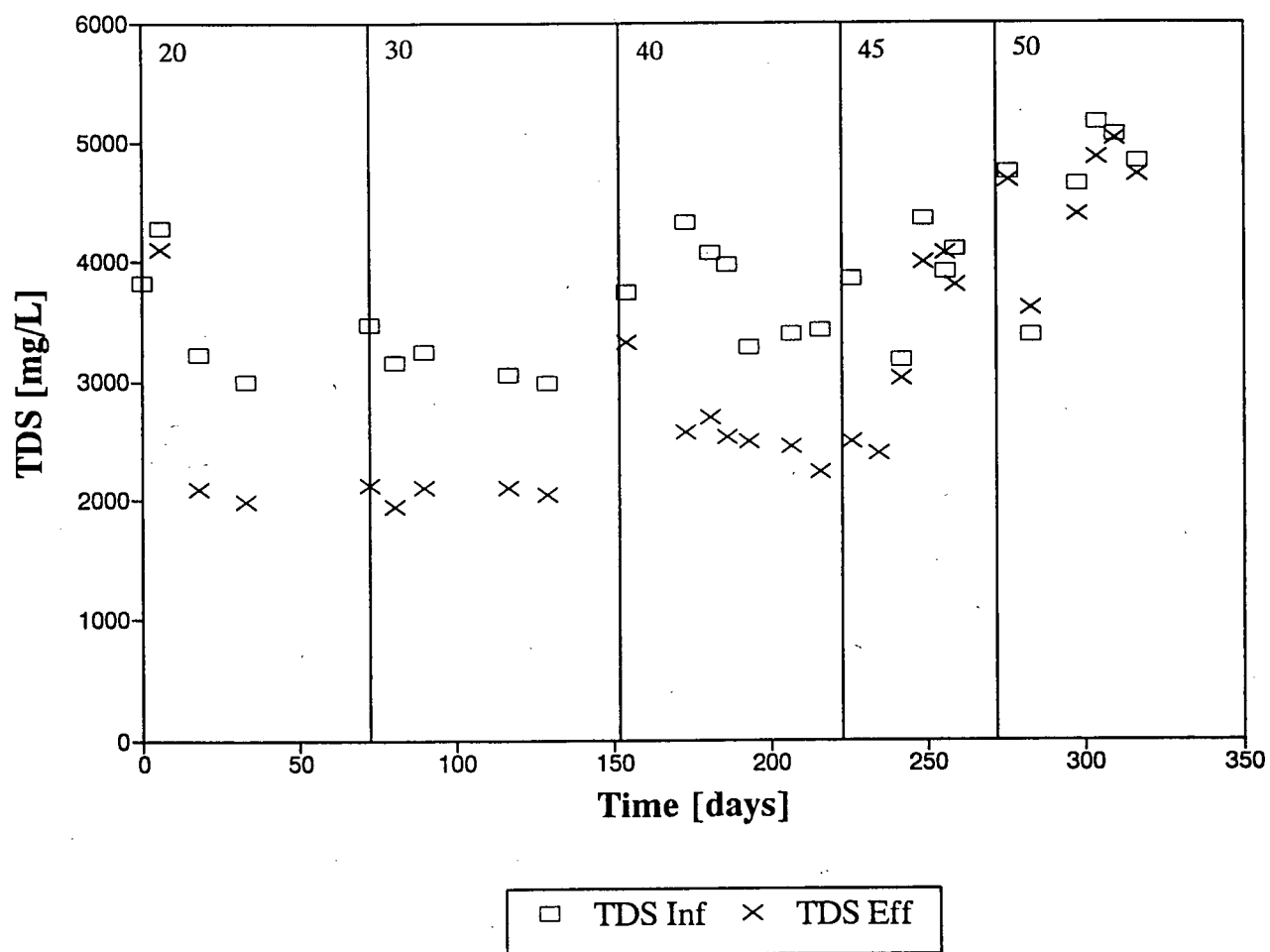


Figure 24. TDS in the influent and effluent of the reactor throughout the experimental period.

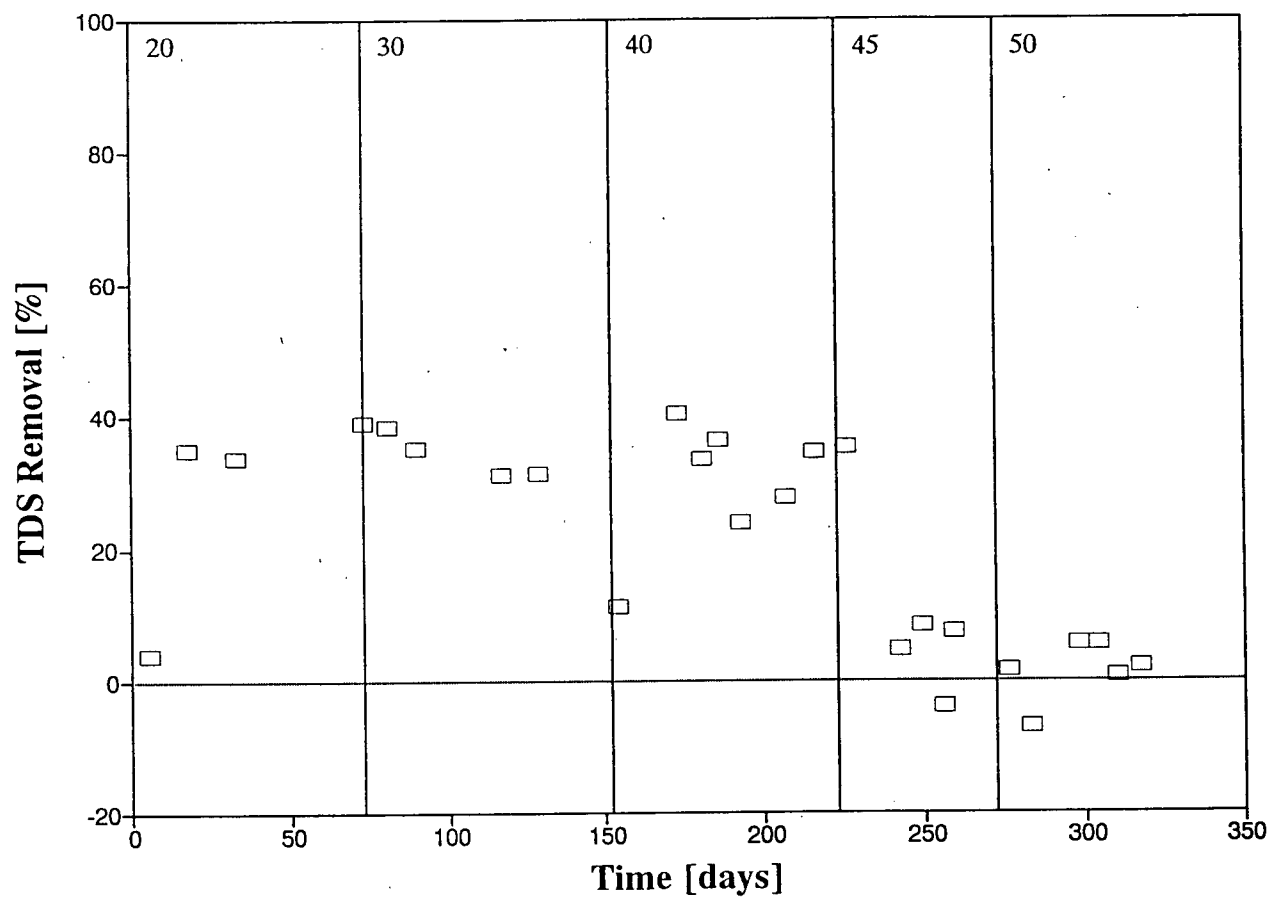


Figure 25. The removal efficiency of TDS throughout the experimental period.

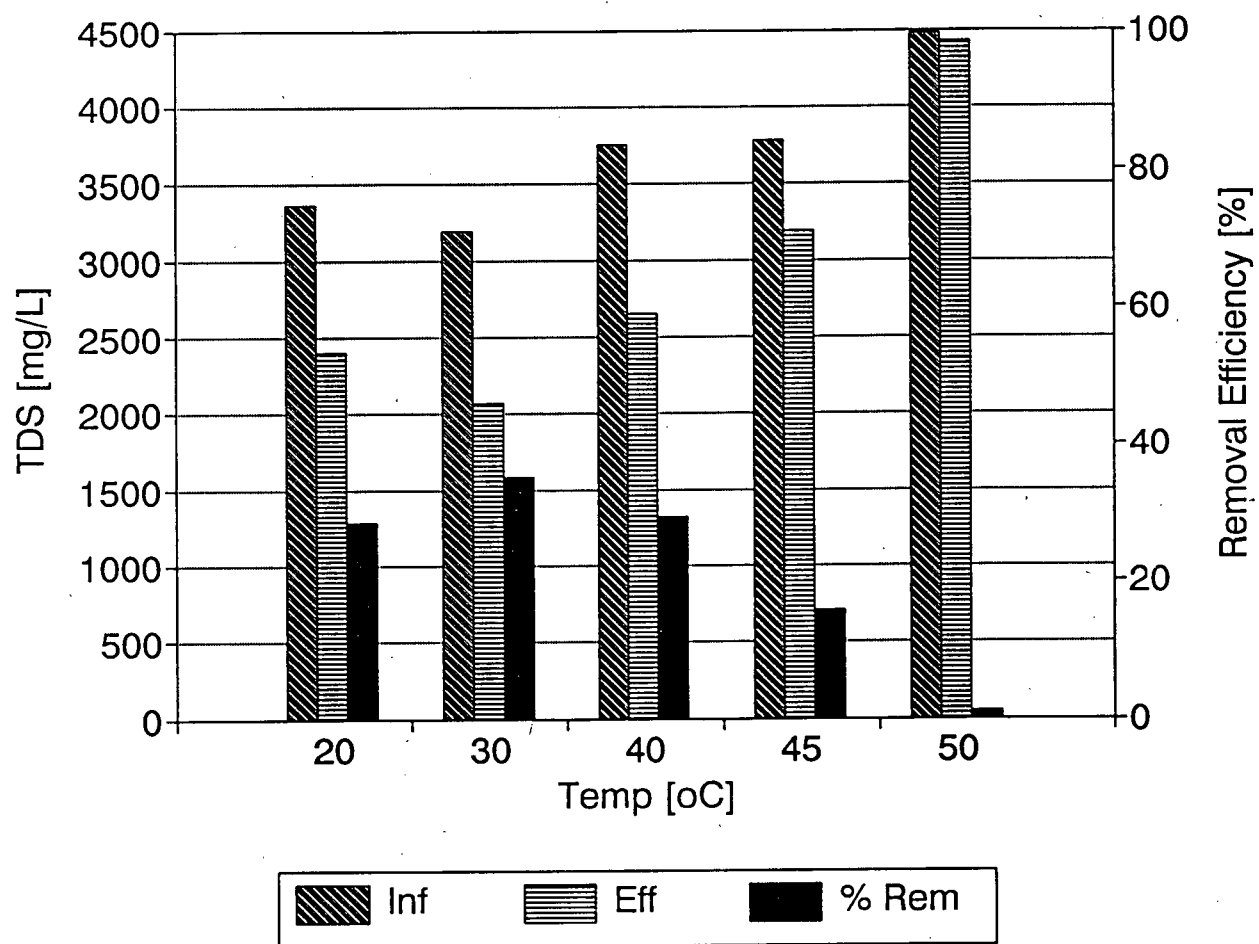


Figure 26. The average TDS influent and effluent concentrations and the removal efficiencies for the different temperature runs.

#### **5.2.2.2. Total Organic Carbon**

In general, the TOC in the influent varied between 3000 and 4500 mg/L (Figure 27). Similar to TDS, TOC was removed in the reactor. The effluent levels were between 200 and 400 mg/L during the 20 and 30°C runs. During the 30 to 40°C transition, higher levels of TOC appeared in the effluent at concentrations above 600 mg/L. The reactor slowly acclimatized to the new temperature as the effluent TOC levels subsequently decreased to about 300 mg/L. During the temperature transition from 40 to 45°C, effluent TOC levels increased only to about 400 mg/L. Soon after the 45°C temperature was attained, the effluent TOC increased to about 800 mg/L and remained approximately 200 mg/L below the influent levels until the end of the experimental period.

The removal efficiency of TOC (Figure 28) reached levels as high as 80% during the 20 and 30°C runs, dropping to about 60% during the 40°C run and sharply falling from 60 to 10% removal during the 45°C run. The TOC removal during the 50°C run was about 10%. As in the case of TDS, the decrease in the TOC removal efficiency (Figure 28) during the 45°C run was similar to the concurrent reactor VSS decrease (Figure 22). Figure 29 summarizes the average influent and effluent concentrations and the removal efficiencies for the different temperature runs.

#### **5.2.2.3. Chemical Oxygen Demand**

The effluent total and dissolved COD was measured during the experimental period (Figures 30 and 31). The influent TCOD varied from 2500 to 5500 mg/L (Figure 30). The effluent TCOD values ranged from 500 to 1000 mg/L during the 20 and 30°C runs, but increased temporarily to over 1500 during the 30 to 40°C temperature change. Generally, effluent levels remained above 1000 mg/L except for one low measurement below 500 mg/L right after the 40 to 45°C transition. During the 45°C run effluent TCOD increased towards the end of the run, this pattern continuing during the 50°C run.

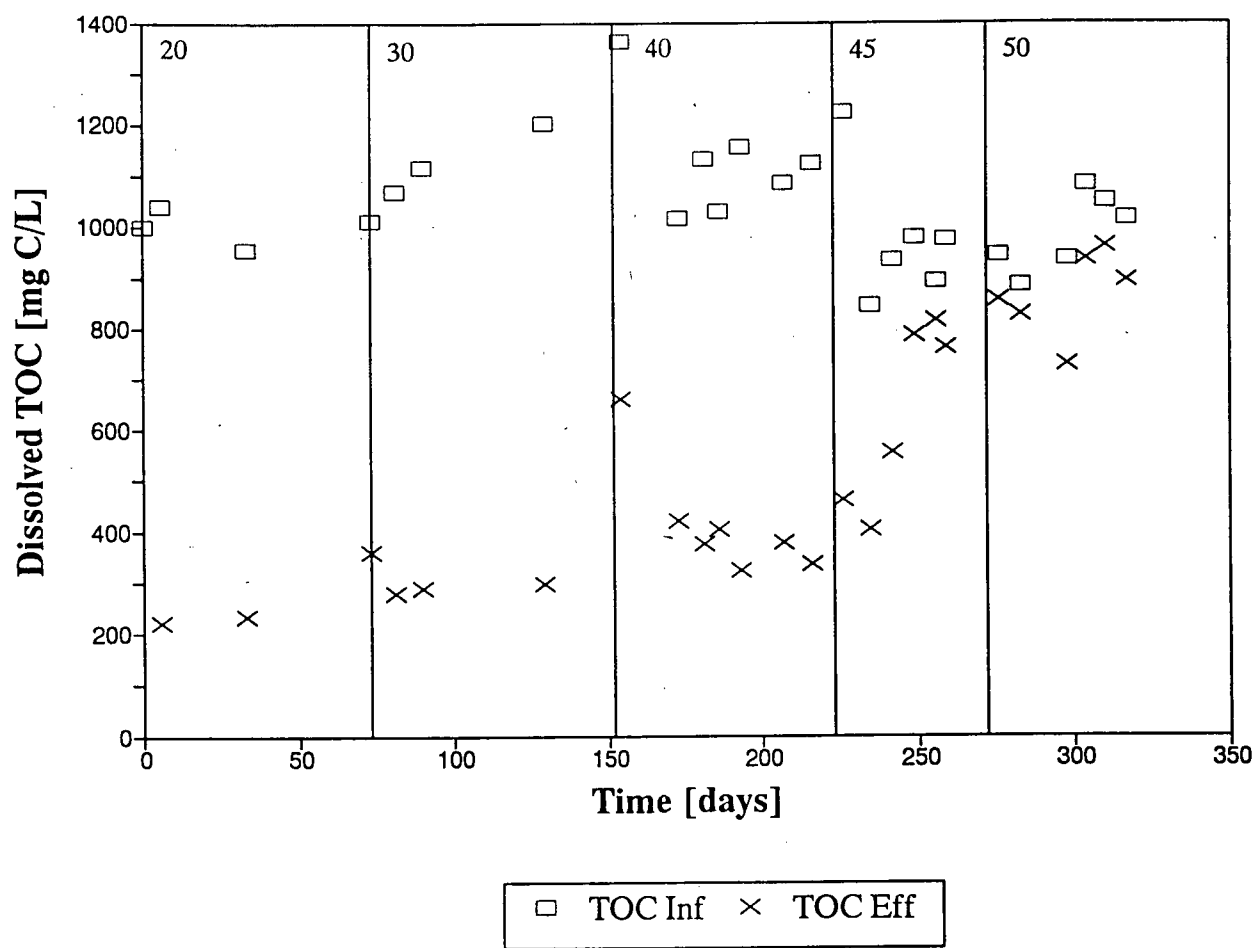


Figure 27. The dissolved TOC in the influent and effluent over the experimental period.



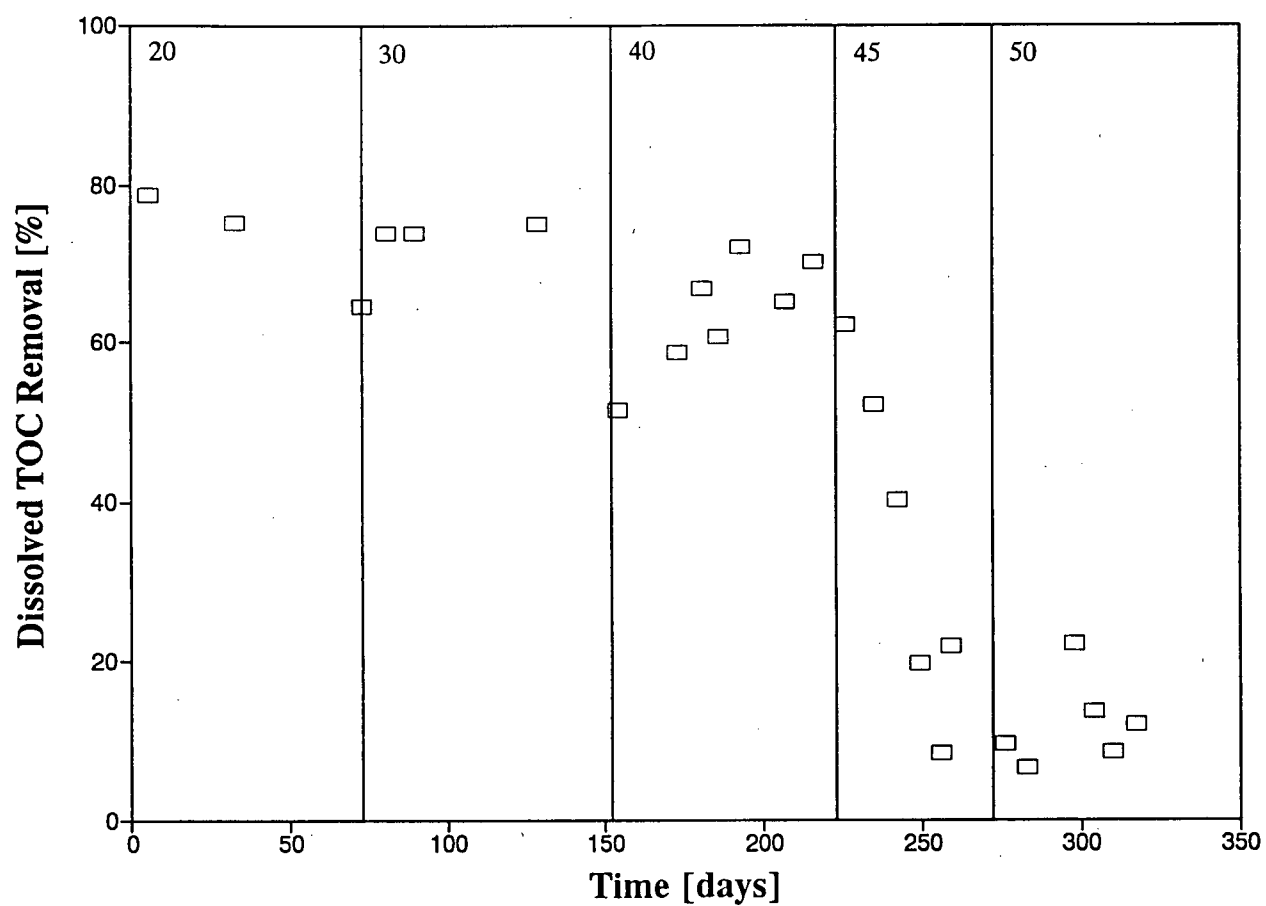


Figure 28. The removal efficiency of TOC throughout the experimental period.

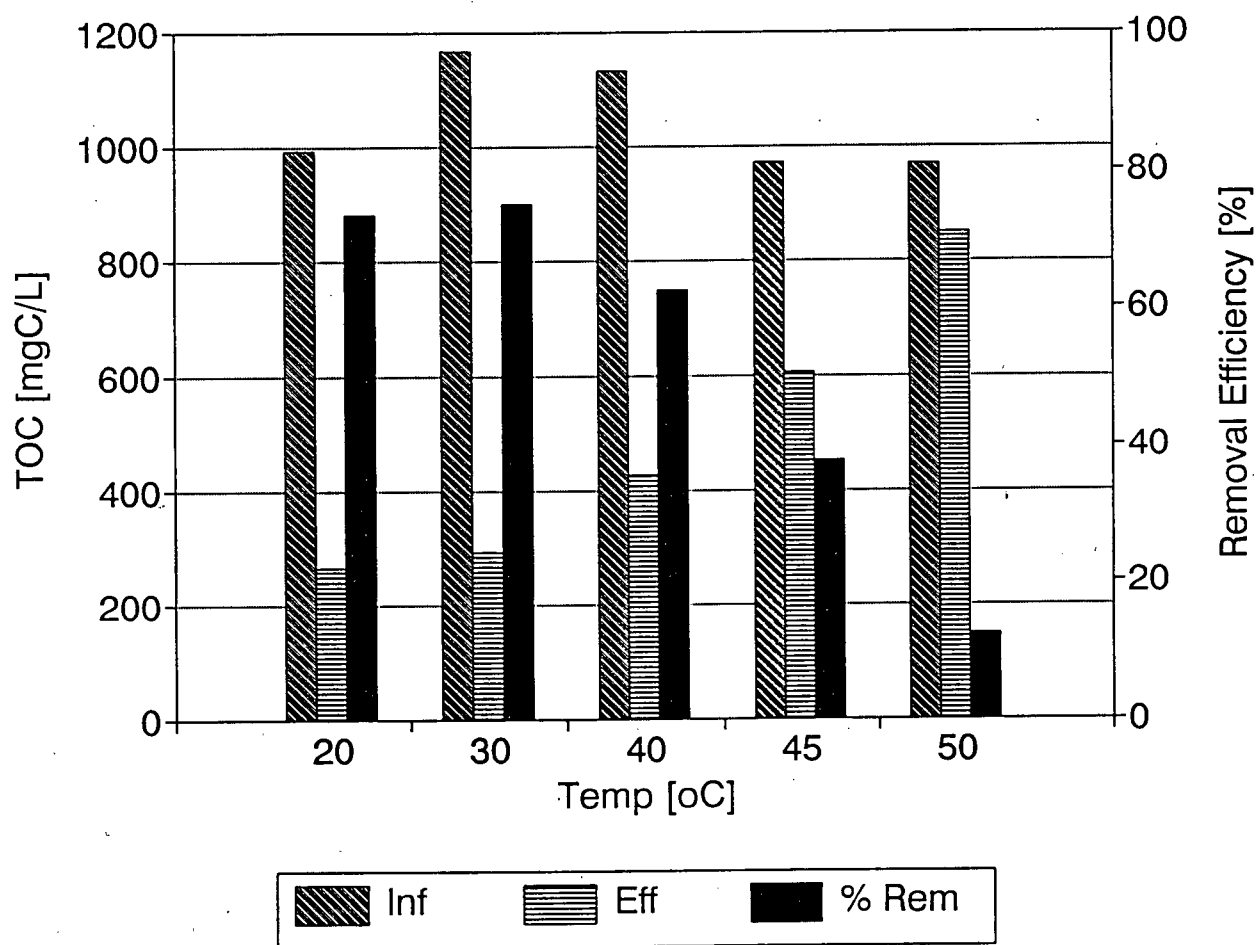


Figure 29. The average TOC influent and effluent concentrations and the removal efficiencies for the different temperature runs.

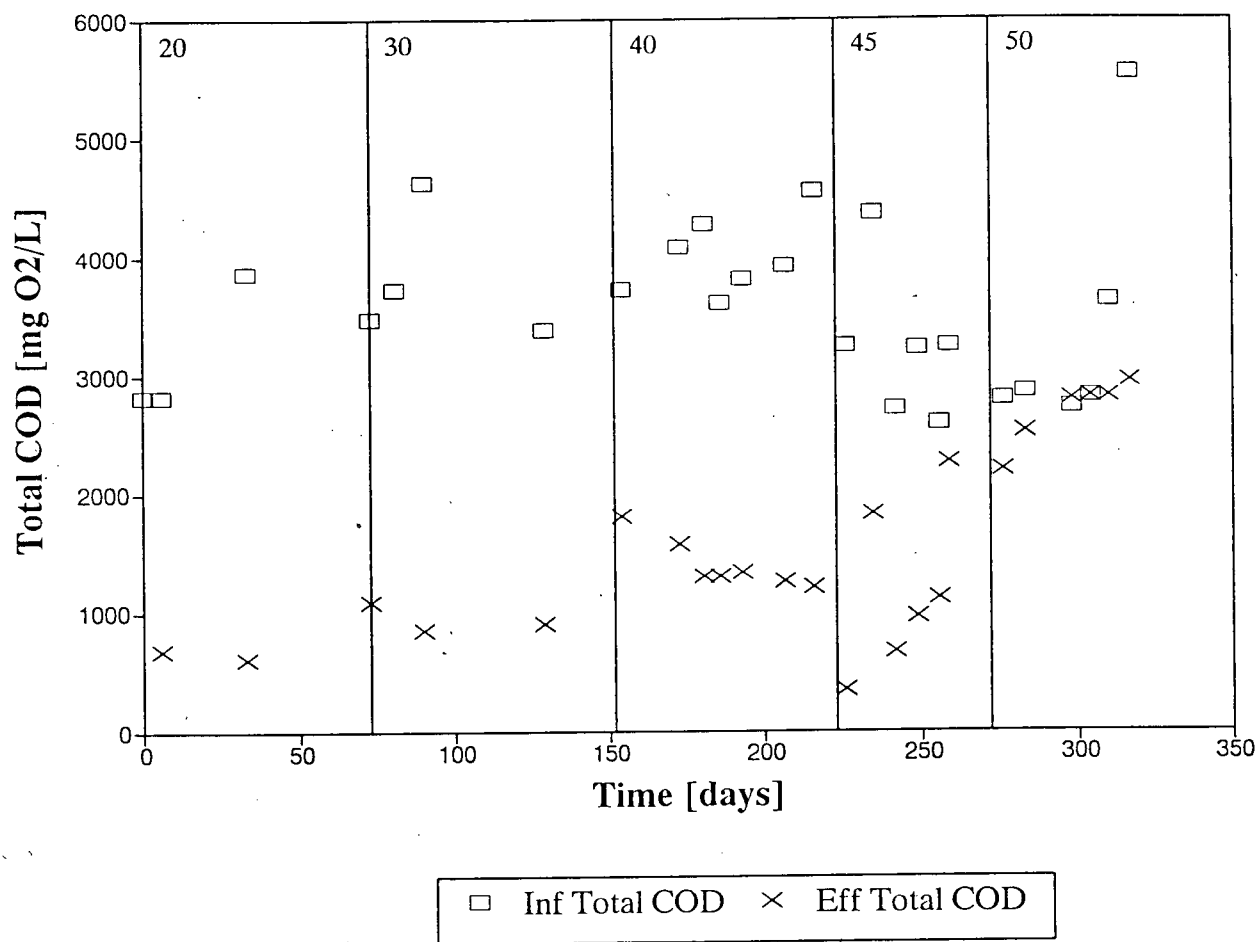


Figure 30. The TCOD in the influent and effluent over the experimental period.

The influent DCOD (Figure 31) exhibited a lower variability of between 2300 and 3100 mg/L than the TCOD because no solids were measured in the DCOD. The same applied to the effluent (Figure 31), but the effluent DCOD levels were similar to, but about 200 mg/L lower than the effluent TCOD levels. Variations in influent TCOD beyond the similar variations of DCOD might be partly due to wood fibres and other pulping residues and biological growth (Figures 30 and 31).

The removal efficiency of TCOD (Figure 32) was about 80% for the 20 and 30°C runs and about 60 to 70% for the 40°C run. The removal efficiency decreased considerably during the 45°C run to about 20%. This decrease in removal continued during the 50°C run until the removal reached zero, then began increasing near the end of the experimental period. The sharp increase in removal near the end of the 50°C run reflected the sharp increase of the TCOD in the influent (Figure 30), most likely caused by high levels of solids growing in the influent bucket observed in the influent VSS measurement (Figure 30) and from visual observations.

The removal efficiency of DCOD (Figure 33) followed a similar pattern to TCOD, except at the end of the experimental period. The sharp increase in removal of TCOD near the end of the 50°C run was not observed in the DCOD results, confirming that the increase seen in the TCOD removals was due to material filtered out in the DCOD measurement which was probably suspended solids accumulating in the influent bucket. Figures 34 and 35 summarize the average influent and effluent concentrations and the removal efficiencies for the different temperature runs for TCOD and DCOD.

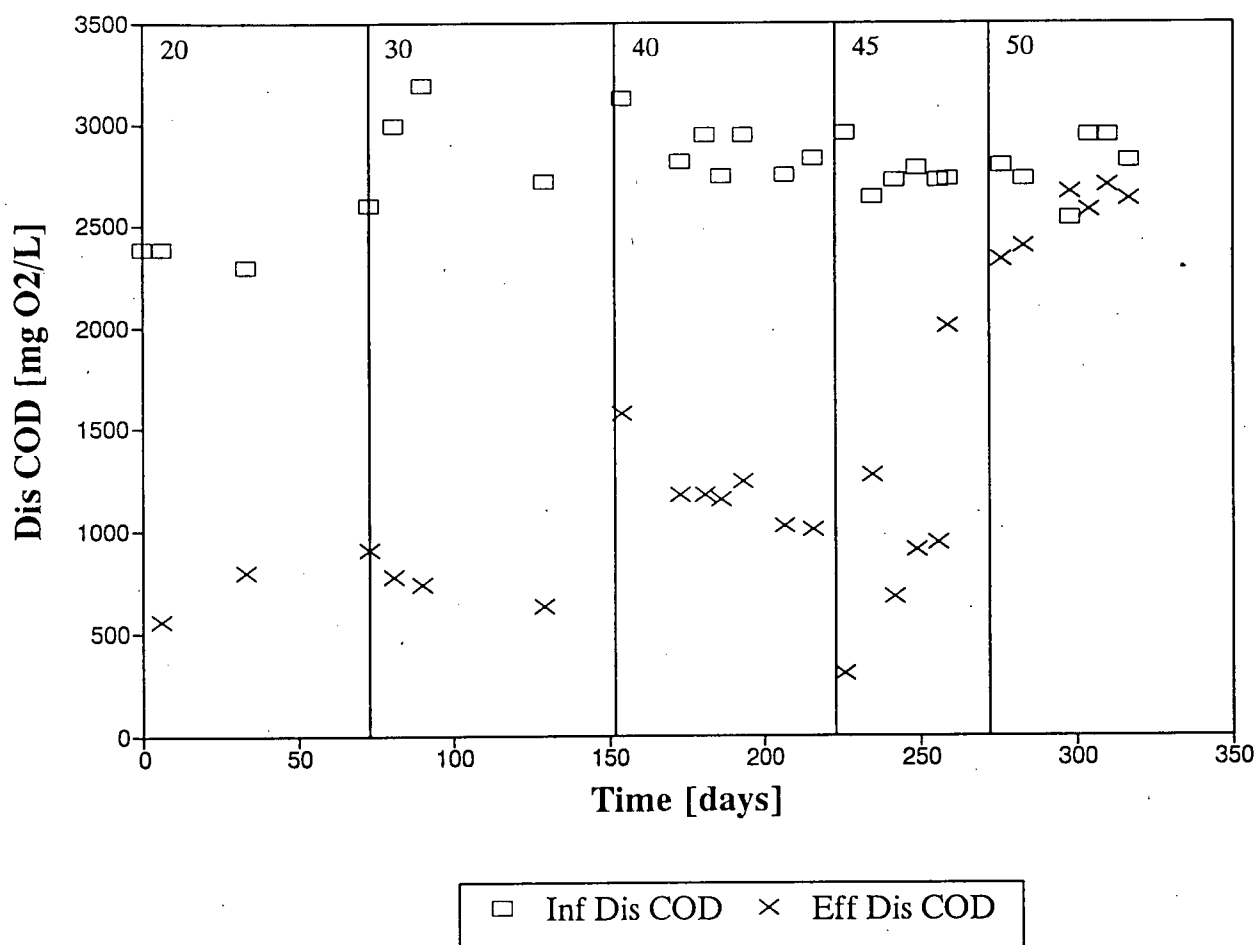


Figure 31. The DCOD in the influent and effluent over the experimental period.

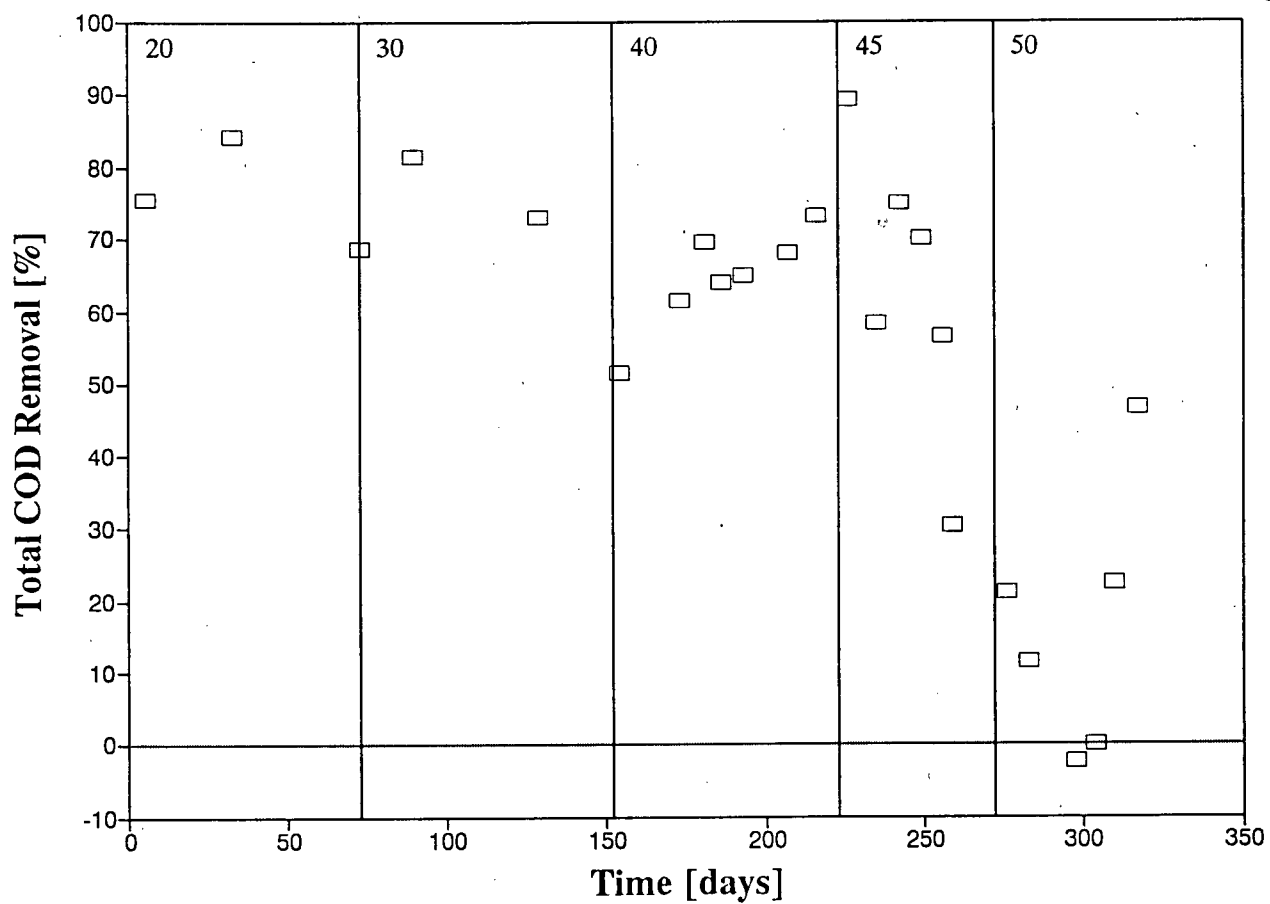


Figure 32. The removal efficiency of TCOD throughout the experimental period.

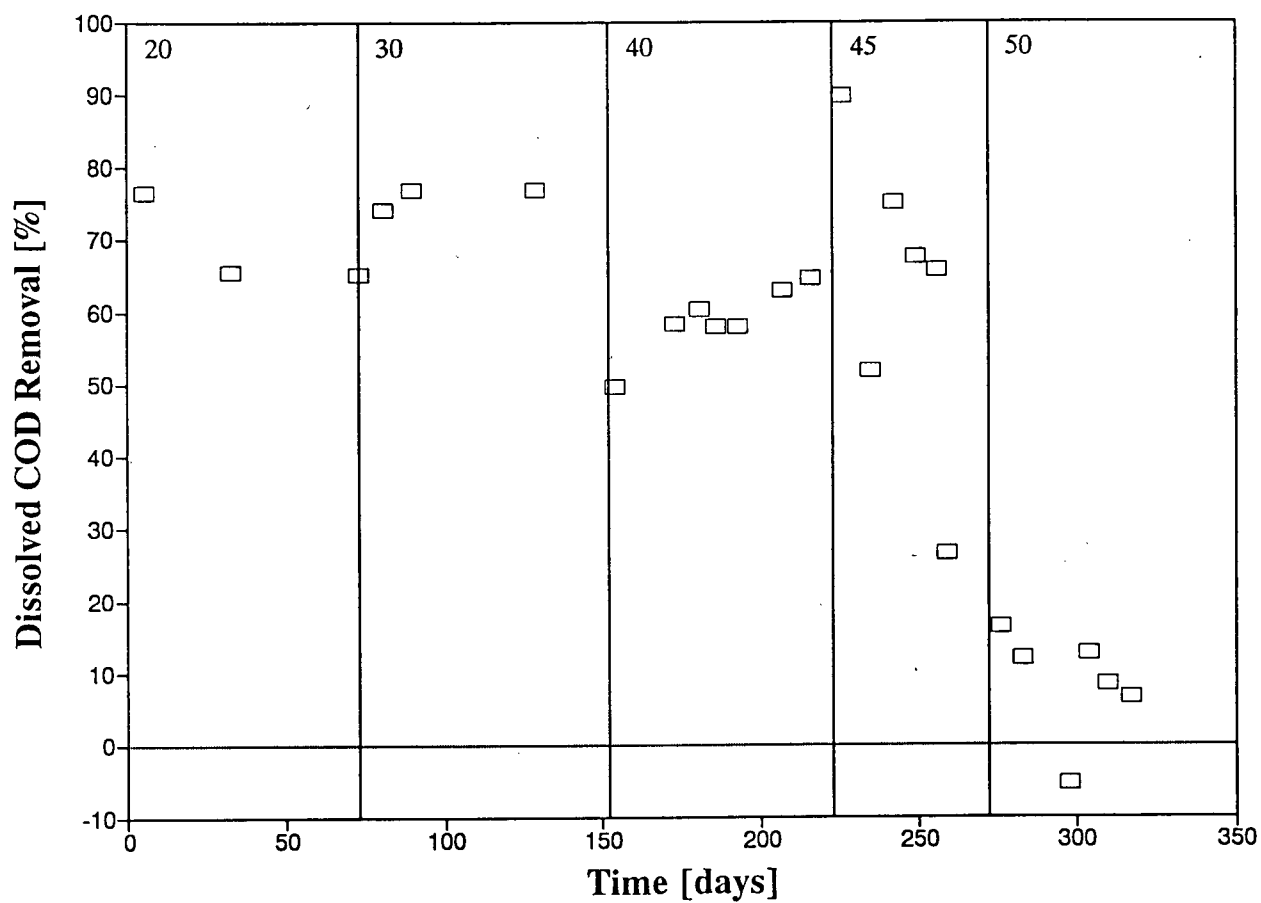


Figure 33. The removal efficiency of DCOD throughout the experimental period.

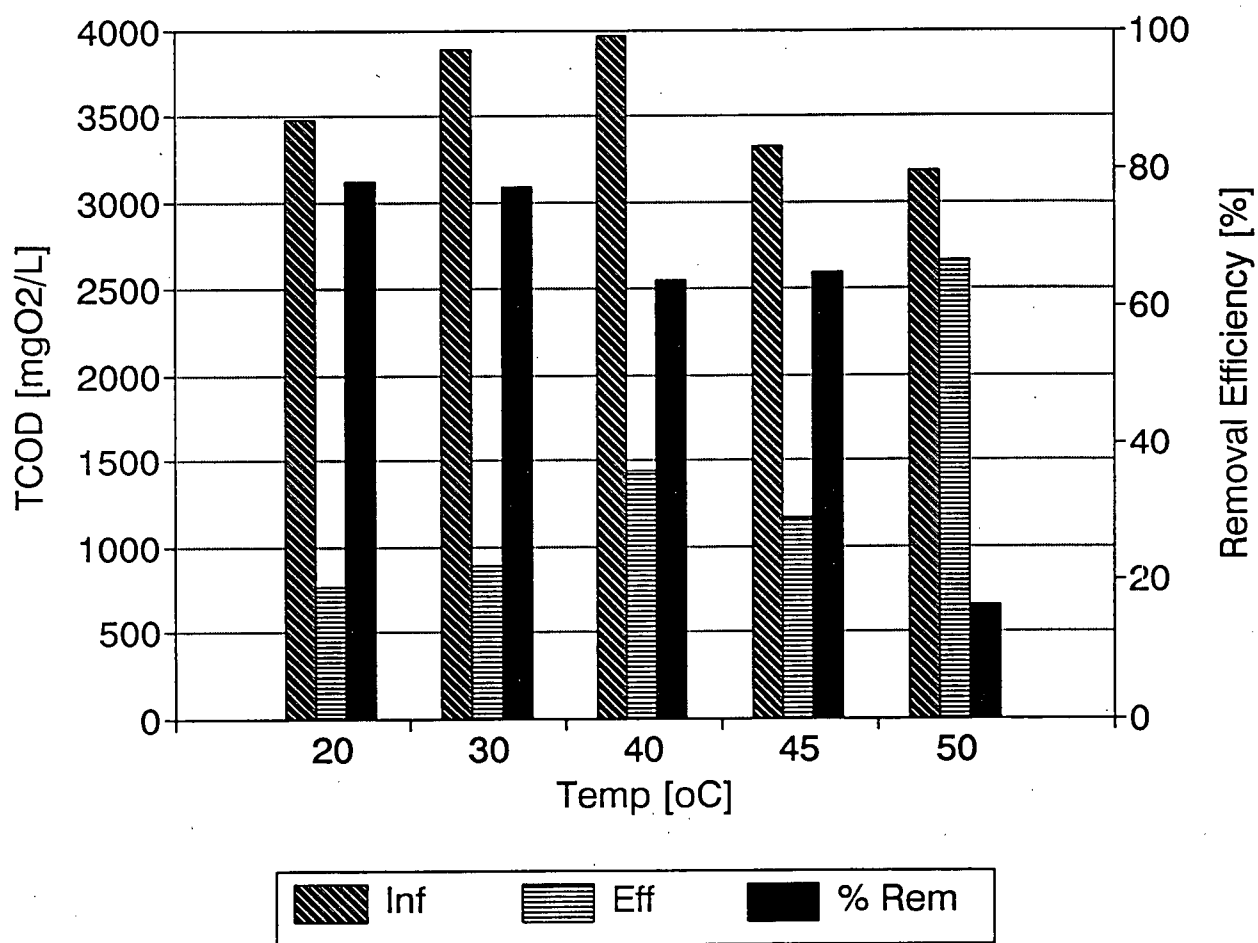


Figure 34. The average TCOD influent and effluent concentrations and the removal efficiencies for the different temperature runs.



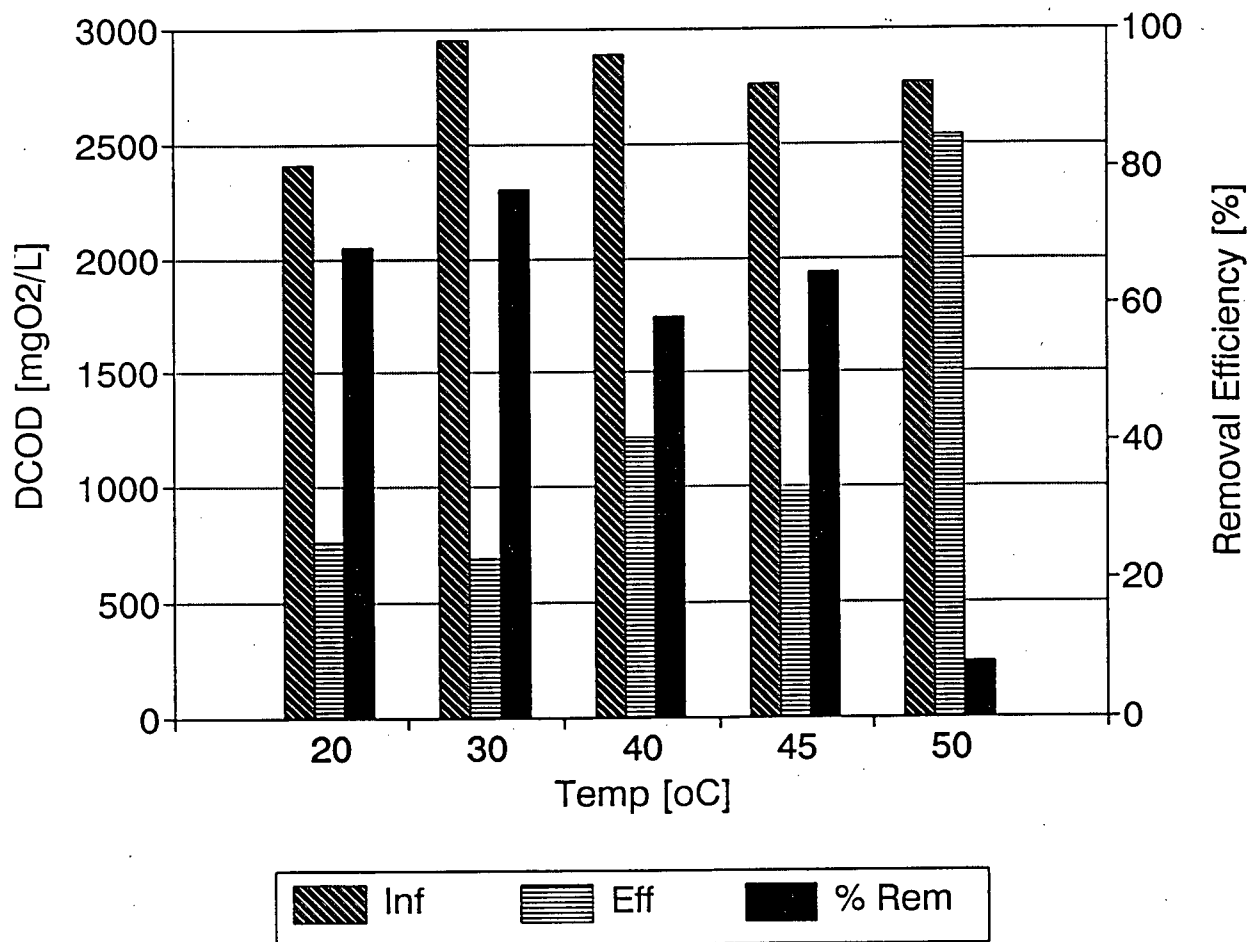


Figure 35. The average DCOD influent and effluent concentrations and the removal efficiencies for the different temperature runs.

### 5.3. Reactor Parameters

#### 5.3.1. Food to Microorganism Ratios and Specific Substrate Utilization Rates

The decrease in the TDS, TOC, TCOD and DCOD removal efficiencies (Figures 25, 28, 22, and 23) observed during the 45°C run might have been caused by the concurrent decrease in reactor VSS (Figure 22). A lower biomass inventory in the reactor might have had reduced substrate removal ability. By taking into account the amount of biomass present in the reactor and the reactor flow and volume, the specific substrate utilization rates for each temperature run better reflect the capabilities of the reactor solids for contaminant removal.

Useful design parameters, the specific substrate utilization rate (U) and the food to microorganism ratio (F/M) are calculated by the following equations (Equations 6 and 7) (Tchobanoglous and Burton, 1991; Benefield and Randall, 1980). They are compared with values reported in the literature to ensure that the treatment was within reasonable control parameters and operational responses. The F/M ratios can be used as a design parameter in a scale-up of this biological process. The U values can be used to check the performance of similar biological processes in future research.

$$U = \frac{Q (S_o - S)}{V_r \cdot X} \quad \text{Eqn. 6}$$

$$F/M = \frac{S_o}{\theta X} \quad \text{Eqn. 7}$$

Where

Q	=	flow rate [L/d]
S	=	final concentration of substrate [g/L]
S <sub>o</sub>	=	initial concentration of substrate [g/L]
X	=	concentration of mixed liquor microorganism [g MLVSS]
θ	=	hydraulic detention time [d]
V <sub>r</sub>	=	reactor volume = 10L

#### **5.3.1.1. Food to Microorganism Ratios**

The food to microorganism (F/M) ratios were calculated for the different temperature runs and for the different substrate measurements (Tables 18 and 19). The increase of F/M values with temperature reflected the decreased MLVSS concentrations and the high influent levels at the end of the 50°C temperature run.

In comparing the F/M ratios in Tables 18 and 19 with other F/M ratios reported in the literature, differences in the measured substrate prevents direct comparison. However, F/M ratios in BOD<sub>5</sub> units reported in the literature can be roughly compared with the measured F/M ratios in TCOD units (Table 19) by dividing the measured values in half. This conversion, derived from the influent TCOD and BOD<sub>5</sub> comparison reported earlier (Table 18), roughly converts the influent TCOD into its BOD<sub>5</sub> equivalent.

The measured F/M ratios for the reactor in this study are higher than those reported for municipal SBR aerobic treatment (Table 20). The high F/M ratios could also be due to a shorter HRT and/or a lower MLVSS level than in municipal SBR aerobic treatment. This was not found to be the case since the MLVSS levels and HRTs of several municipal waste treatment plants using SBR technology were generally similar or lower than those of the reactor in this study. The high F/M ratios are probably due to the nature of the feed in the bioreactor, being a high strength waste, rather than a less-concentrated municipal waste.

Table 21 lists typical F/M ratio values for several modifications of the conventional activated sludge treatment process for municipal waste. The measured F/M ratios in Table 19, after dividing them in half to roughly convert them to BOD<sub>5</sub> units, fall within the range of the SBR typical values in Table 21.

Table 18. The food to microorganism ratios (F/M) for the substrates TDS and TOC for the different temperature runs during the experimental period.

Temp	F/M [mg S <sub>o</sub> / mg MLVSS · d]									
[°C]	TDS					TOC				
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n
20	0.41	0.01	0.40	0.42	2	0.11	0.01	0.10	0.13	2
30	0.30	0.02	0.27	0.32	4	0.10	0.08	0.09	0.11	4
40	0.39	0.03	0.34	0.43	7	0.12	0.01	0.09	0.13	7
45	0.59	0.16	0.39	0.79	5	0.14	0.03	0.08	0.19	6
50	1.25	0.21	0.92	1.51	6	0.27	0.04	0.21	0.32	6

Table 19. The food to microorganism ratios (F/M) for the substrates TCOD and DCOD for the different temperature runs during the experimental period.

Temp	F/M [mg S <sub>o</sub> / mg MLVSS · d]									
[°C]	TCOD					DCOD				
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n
20	0.40	0.12	0.28	0.51	2	0.27	0.03	0.24	0.30	2
30	0.35	0.06	0.30	0.45	4	0.27	0.03	0.23	0.31	4
40	0.42	0.06	0.35	0.53	7	0.30	0.02	0.26	0.33	7
45	0.45	0.10	0.33	0.63	6	0.39	0.10	0.25	0.53	6
50	0.94	0.37	0.63	1.73	6	0.76	0.10	0.58	0.88	6

Table 20. The F/M ratios, MLVSS concentrations, and HRTs of several municipal waste treatment plants using SBR technology. Plant A was converted to SBR treatment from conventional continuous flow activated sludge treatment (Irvine *et al.*, 1983). Plants B and C were converted to SBR treatment from extended aeration and plant D was converted from septic tanks (Melcer *et al.*, 1987). The range of F/M ratios at 20°C for the reactor in this study (Reactor) are listed for comparison.

Plant	A	B	C	D	Reactor
F/M [g BOD <sub>5</sub> / g MLVSS · d]	0.12	0.041	0.062	0.308	
F/M [g TCOD / g MLVSS · d]					0.28 - 0.51
MLVSS [mg/L]	1380	3180	1477	2387	
HRT [d]	0.34	2.1	0.63	0.32	

Typical F/M design parameters for various pulp mill biotreatment systems are listed in Table 22. The measured F/M values for TCOD, after they are divided in half to roughly convert to BOD<sub>5</sub> substrate, are similar to the aerated stabilization basin (ASB), activated sludge, and oxygen-activated sludge biotreatment processes. As seen from similar values in Tables 21 and 22, the reactor in this study operated under reasonable F/M parameters.

Table 21. Typical values of F/M ratios for different modifications of conventional activated sludge treatment (Tchobanoglous and Burton, 1991). The range of F/M ratios at 20°C for the reactor in this study (Reactor) are listed for comparison.

Process Modification	F/M [g BOD <sub>5</sub> / g MLVSS · d]
Conventional plug flow	0.2 - 0.4
Complete-mix	0.2 - 0.6
Step-feed	0.2 - 0.4
Modified aeration	1.5 - 5.0
Contact stabilization	0.2 - 0.6
Extended aeration	0.05 - 0.15
High-rate aeration	0.4 - 1.5
Kraus process	0.3 - 0.8
High-purity oxygen	0.25 - 1.0
Oxidation ditch	0.05 - 0.30
Sequencing batch reactor	0.05 - 0.30
Deep shaft reactor	0.5 - 5.0
Reactor [g TCOD / g MLVSS · d]	0.28 - 0.51

Table 22. F/M design parameters for various pulp mill biotreatment systems (Springer, 1986).

Biotreatment System	F/M
	[mg BOD <sub>5</sub> / mg MLVSS · d]
ASB	0.1
Activated Sludge	0.3 - 0.5
Extended Aeration	0.1
Oxygen-activated Sludge	0.7
Rotating Biological Surface	1.0

#### 5.3.1.2. Specific Substrate Utilization Rates

The specific substrate utilization rates (U), also called substrate utilization ratios, were calculated for the different temperature runs and for the different substrate measurements of TDS, TOC, TCOD, and DCOD (Tables 23 and 24). The U values for all substrates were similar for the 20, 30, and 40°C temperature runs. The U values of TDS and TOC were lower at the higher temperatures of 45 and 50°C. The U values of TCOD and DCOD were similar to those of lower temperatures at 45°C, but were lower during the 50°C temperature run.

In comparing the U values in Tables 23 and 24 with other U values reported in the literature, differences in the measured substrate prevents direct comparison. However, U values from BOD<sub>5</sub> removal can be roughly compared with the measured U values from COD removal since they are both types of oxygen demands. Table 25 allows a comparison of U values with various pulp mill biotreatment systems. The measured U values (Table 24) are closest to those of activated sludge (Table 25).

Table 23. The specific substrate utilization rates (U) for the substrates TDS and TOC for the different temperature runs during the experimental period.  $S_r$  = Substrate removed.

Temp	U [mg $S_r$ / mg MLVSS · d]									
[°C]	TDS					TOC				
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n
20	0.08	0.06	0.02	0.13	2	0.09	0.01	0.08	0.10	2
30	0.11	0.01	0.08	0.12	4	0.07	0.01	0.06	0.08	4
40	0.12	0.04	0.04	0.16	7	0.07	0.01	0.06	0.09	7
45	0.00	0.12	-0.23	0.14	6	0.04	0.02	0.01	0.08	6
50	0.02	0.05	-0.06	0.08	6	0.03	0.01	0.02	0.05	6

Table 24. The specific substrate utilization rates (U) for the substrates TCOD and DCOD for the different temperature runs during the experimental period.  $S_r$  = Substrate removed.

Temp	U [mg $S_r$ / mg MLVSS · d]									
[°C]	TCOD					DCOD				
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n
20	0.32	0.11	0.21	0.43	2	0.19	0.01	0.18	0.20	2
30	0.29	0.07	0.21	0.37	4	0.20	0.03	0.15	0.24	4
40	0.27	0.06	0.18	0.39	7	0.18	0.02	0.14	0.21	7
45	0.27	0.05	0.19	0.34	6	0.24	0.07	0.13	0.32	6
50	0.21	0.28	-0.02	0.81	6	0.07	0.05	-0.03	0.12	6



Table 25. U design parameters for various pulp mill biotreatment systems (calculated from data from Springer, 1986). The range of U values at 20°C for the reactor in this study (Reactor) are listed for comparison.

Biotreatment System	U [ mg BOD <sub>5</sub> / mg MLVSS · d]
ASB	0.08-0.09
Activated Sludge	0.24 - 0.43
Extended Aeration	0.08
Oxygen-activated Sludge	0.63
Rotating Biological Surface	0.85
Reactor [mg TCOD / mg MLVSS · d]	0.21 - 0.43

A bench-scale activated sludge treatment for TMP wastewater had U values ranging from 0.16 to 0.26 [mg BOD<sub>5</sub> / mg MLVSS · d] for non-filamentous growth and from 0.38 to 0.47 [mg BOD<sub>5</sub> / mg MLVSS · d] for filamentous growth (Liver *et al.*, 1993). Some typical U values for municipal waste treatment are 0.38 [mg BOD<sub>5</sub> / mg MLVSS · d] for conventional activated sludge and 0.12 [mg BOD<sub>5</sub> / mg MLVSS · d] for extended aeration (Wilson, 1981), both comparable to the U values measured here (Table 24).

In conclusion, the specific substrate utilization rates for the reactor in this study were similar to those of other municipal and pulp mill treatment processes. In general, U values at high temperatures were lower than those at lower temperatures, indicating a lower substrate removal despite the lower MLVSS concentrations at higher temperatures. Thus, treatment was not as effective at temperatures above 40°C as the treatment at temperatures of 40°C and below.

### 5.3.2. Growth Yield

Another important consideration in the applicability of this treatment system is the extent of sludge production and the efficiency of the substrate removal. The removal efficiencies between influent and effluent are one way of indicating biodegradation. Removal efficiencies, although valuable operational assessments, do not take into account the material removed during wasting and the internal fluctuations within the reactor. The growth yield (Y) takes into account the total cumulative amount of substrate consumed and the total cumulative amount of MLVSS produced (Equation 8) over a reasonably long period of time.

$$Y = \frac{\text{mass of MLVSS formed}}{\text{mass of substrate removed}} \quad \text{Eqn. 8}$$

The total masses of MLVSS formed during the individual experimental runs were calculated from Figure 23 by subtracting the initial cumulative net biomass growth amount from the final net biomass for that temperature run. The total mass of substrate consumed was determined in a similar manner from cumulative substrate mass flow calculations (Figures A1, A2, A3, and A4 in Appendix A) using the cumulative total substrate removal curve for each temperature run. The calculated growth yield values are listed in Table 26.

Since the SRT was quite variable, but long, the growth yield or the quantity of suspended solids produced per unit mass of substrate was very low. As the reactor biomass grew, substrate was removed from the feed. However, the low growth yields and the high SRT indicates that the sludge was bordering on auto-oxidation. This was advantageous to keep the solids production down to reduce the need to manage the wastes resulting from applying this treatment. At high temperatures of 40 and 50°C, the Y values were negative, indicating little or no substrate removal even after taking account of the reactor biomass level changes.

Table 26. The biomass growth yields during the experimental runs.

Temperature [°C]	Growth Yield		
	for TOC	for TCOD	for DCOD
	[mg VSS/mg C]	[mg VSS/mg O <sub>2</sub> ]	[mg VSS/mg O <sub>2</sub> ]
20	0.29	0.077	0.13
30	0.25	0.073	0.10
40	-0.012	-0.003	-0.005
45	0.11	0.018	0.022
50	-0.25	-0.059	-0.14

The growth yield values during the 20 and 30°C runs were comparable to those observed in the ANAMET treatment process (Table 2) even though this process includes an anaerobic stage. But the measured growth yield at these temperatures were lower than those from aerobic SBR treatment of landfill leachate.(0.87 mg MLSS / mg TOC [C], SRT 19.5 days, Ying *et al.*, 1986). Table 27 lists typical values of growth yield coefficients for conventional biological treatment of different substrates, expressed in units of BOD<sub>5</sub>. In comparing the Y values in Table 26 with other Y values reported in the literature, differences in the form of substrate measured prevents direct comparison. However, Y values from BOD<sub>5</sub> removal can be roughly compared with the measured Y values from COD removal since they are both types of oxygen demands. The growth yield values for the reactor in this study were not as high as those reported for domestic waste activated sludge, being one order of magnitude lower. Growth yield for the reactor in this study was in the order of magnitude of anaerobic digestion. Thus, the growth yield values were lower than for activated sludge domestic waste treatment, but were comparable to anaerobic digestion (Figure 27).

Table 27. Typical values of growth yield for conventional treatment of different substrates (Tchobanoglous and Burton, 1991). The growth yield value calculated for the reactor in this study at 20°C is listed for comparison.

Process	Growth Yield [mg VSS / mg BOD <sub>5</sub> ]	
	Range	Typical
<b>Activated Sludge:</b>		
Domestic waste	0.4 - 0.8	0.6
<b>Anaerobic Digestion:</b>		
Domestic waste	0.040 - 0.100	0.060
Fatty acids	0.040 - 0.070	0.050
Carbohydrates	0.020 - 0.040	0.024
Protein	0.050 - 0.090	0.075
Reactor [mg VSS / mg TCOD]		0.077

### 5.3.3. Summary of Significance of Reactor Parameters

Overall, F/M ratios were similar from 20 to 45°C and comparable to values in the literature, while at 50°C, the ratio was higher. This was probably due to the high-strength waste treated. U values using TDS and TOC as substrates were similar from 20 to 40°C and U values using TCOD and DCOD were similar from 20 to 45°C and comparable to values in the literature. At higher temperatures, the U values decreased. This indicated that the decrease in substrate removals with increasing temperatures was not merely due to the decrease in reactor biomass, but also to a reduced ability to remove contaminants at high temperatures.

Growth yield values (Y) were similar at the lower temperatures of 20 and 30°C and comparable to values in the literature, but decreased at higher temperatures. This indicated

that during periods of lower substrate removal, at higher temperatures, the biomass was not converting substrate into biomass as efficiently as at lower temperatures. Thus, the lower sludge production would be an advantage for treatment at high temperatures.

In looking at the removal efficiencies and substrate utilization rates of conventional substrates such as TDS, TOC, TCOD, and DCOD, and in taking into account the change in reactor biomass, effective removal can be achieved at temperatures up to 40 for COD removal and up to 45°C for TDS and TOC removal. Thus, in conclusion, at higher temperatures, maintenance of an active biomass is difficult and the treatment efficiency is low.

#### **5.4. Resin and Fatty Acids Behaviour in the Reactor During the Experimental Period**

##### **5.4.1. Resin and Fatty Acids Removal**

Even though they account for less than 5% of the TOC in the reactor, the behaviour of resin and fatty acids under high temperature SBR treatment was investigated because they are partially responsible for problems in whitewater recirculation. The removal efficiencies and removal rates of resin and fatty acids were examined to investigate the efficiency of the reactor. As can be seen in more detail in the following sections, the resin and fatty acids were removed to varying degrees within the reactor. Removal does not necessarily mean that biological degradation occurred. Possible alternative processes that might have occurred, such as chemical oxidation during aeration and accumulation in the solids, were also investigated.

##### **5.4.1.1. Resin and Fatty Acids Removal Efficiency Between the Influent and Effluent**

Resin and fatty acids were removed to different extents at the different steady state temperatures. Figure 36 shows the total fatty acid concentration of the influent and effluent and Figure 37 shows the total resin acids concentration of the influent and effluent.

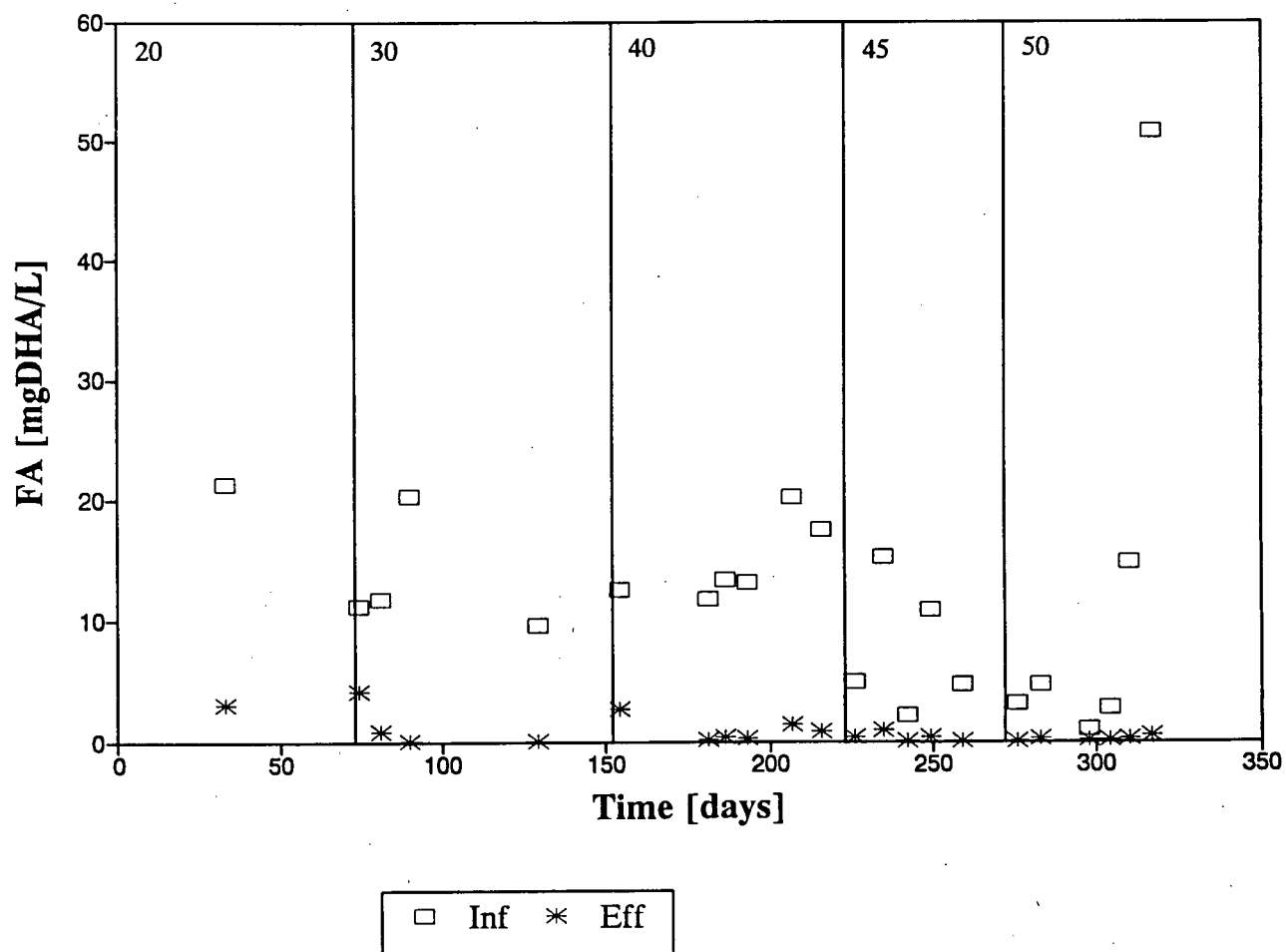


Figure 36. The total fatty acid concentrations of the influent and effluent during the experimental period.

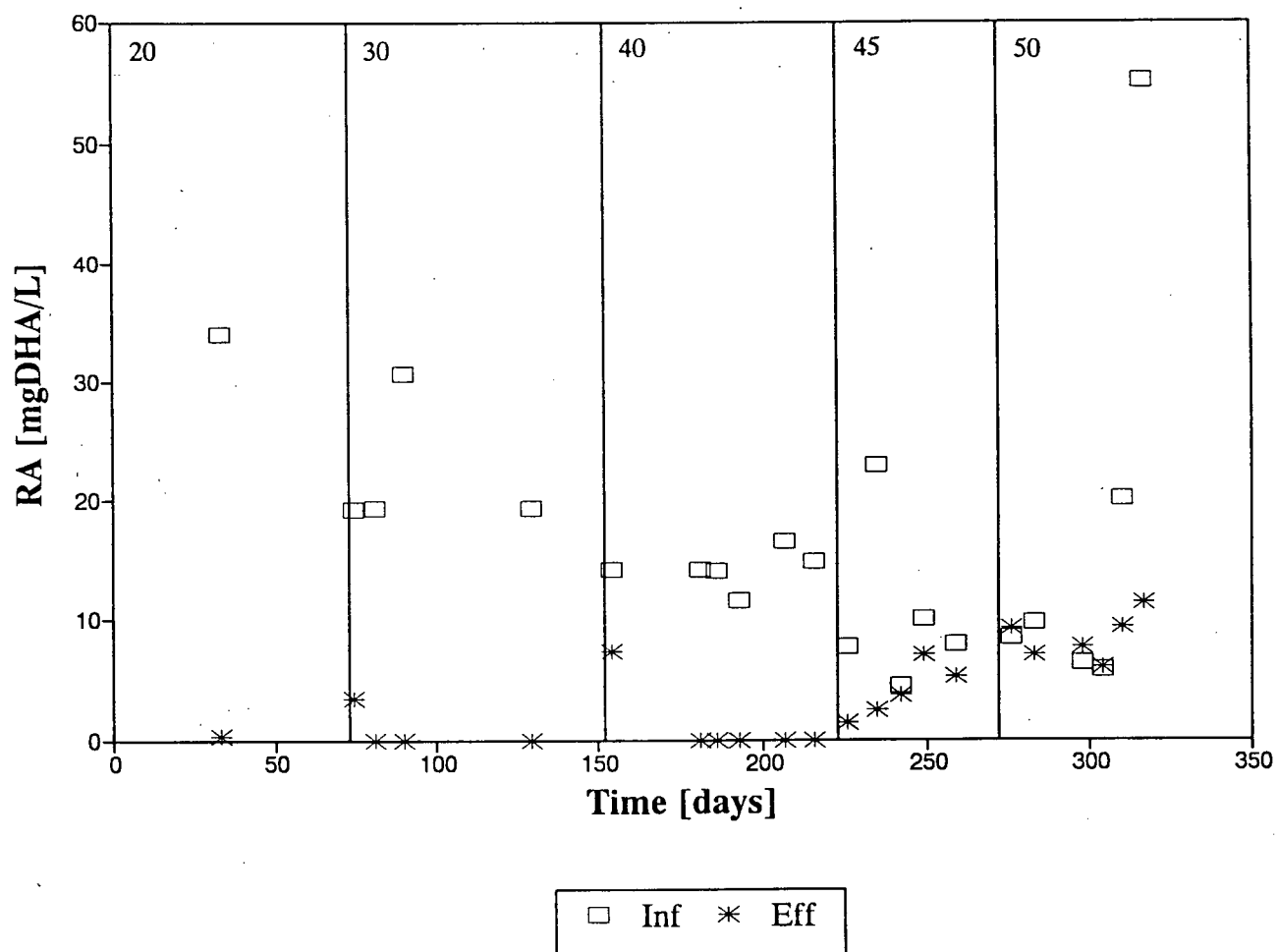


Figure 37. The total resin acids concentrations of the influent and effluent during the experimental period.

Influent RFA values (Figures 36 and 37) appeared to decrease throughout the experimental period. This apparent decrease is probably due to the higher than average concentrations near the beginning of the experimental period in the screw pressate (Figures 18 and 19). The low influent RFA levels during the 45°C run and at the beginning of the 50°C temperature run (Figure 36 and 37) did not coincide with high influent VSS measurements (Figure 20) so most likely were not due to biological RFA removal in the influent bucket.

At the end of the 50°C temperature run, one influent resin and fatty acid measurement was considerably greater than previous influent levels (Figures 36 and 37). Although the end of the 50°C run coincides with the changeover from an old screw pressate batch to a new screw pressate batch, the resin and fatty acid values of both batches were comparable (Figures 17, 18, and 19). The measurement point, coincides with high solids levels in the influent (Figure 20) and high TCOD levels contrasted with normal DCOD levels (Figures 30 and 31). At times during the experimental period, influent solids were at levels similar to those at the end of the 50°C run, but influent characteristics were not drastically different then as they were at the end of the 50°C run. Resin and fatty acid levels, especially fatty acids, in the mixed liquor liquid at the beginning of the react cycle were much higher than previous levels. Thus, the high resin and fatty acid concentration is not attributable solely to solids accumulated in the influent bucket that were high in resin and fatty acids. Since this was measured in only one point near the end of the experimental period where it had not been affecting the reactor for long, minimal weight is given in the following discussion to this measurement.

Effluent fatty acids levels were near zero throughout all of the temperature runs (Figure 36). The fatty acid removal efficiencies were generally higher than 90% throughout all of the temperature runs, except during temperature transitions (Figure 38). Some removal efficiencies were low because of the lower influent values during the 45 and 50°C temperature runs.



Although effluent resin acids concentrations (Figure 37) were near zero during the 20, 30 and 40°C temperature runs, they began to increase after the 45°C temperature transition. Resin acids consistently appeared in the effluent during the 45 and 50°C temperature runs. The resin acids removal efficiencies (Figure 39) were essentially 100% at the lower temperatures, then varied from -20% to 90% removal during the higher temperature runs.

Low influent resin and fatty acid concentrations, such as those near the end of the 45°C run and at the beginning of the 50°C run, resulted in lower calculated removal efficiencies. In cases where the resin or fatty acids were removed completely, there might have been potential for even greater mass removal had more resin or fatty acids been present. The influent and effluent concentrations of resin acids and fatty acids and their percent removals are summarized in Figures 40 and 41.

The calculation of removal efficiency is partially affected by the amount of material available for removal. Thus mass removals better reflect the actual amount of resin and fatty acids removed. The mass removals for both resin and fatty acids decreased with increasing temperature (Figure 42). Since resin acids were present in the effluent at high temperatures (Figure 37), this mass removal trend shows a diminished ability to remove resin acids. Fatty acids, on the other hand, are not present in the effluent at high temperatures (Figure 36) and thus the decreasing mass removals might reflect lower fatty acid concentrations in the influent with higher temperatures (Figure 40) rather than a decreased ability to remove fatty acids.

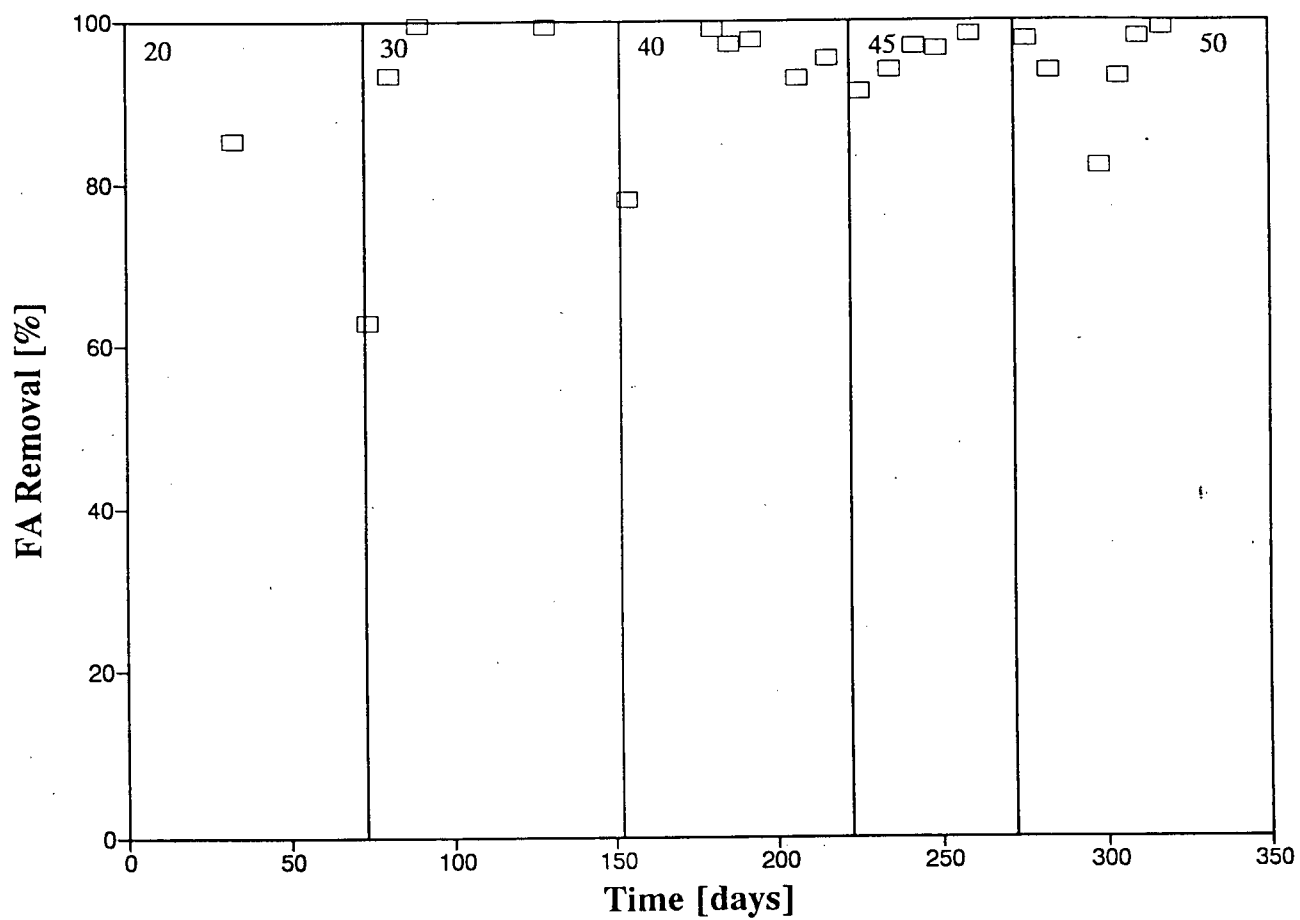


Figure 38. The removal efficiencies of the total fatty acids during the experimental period.

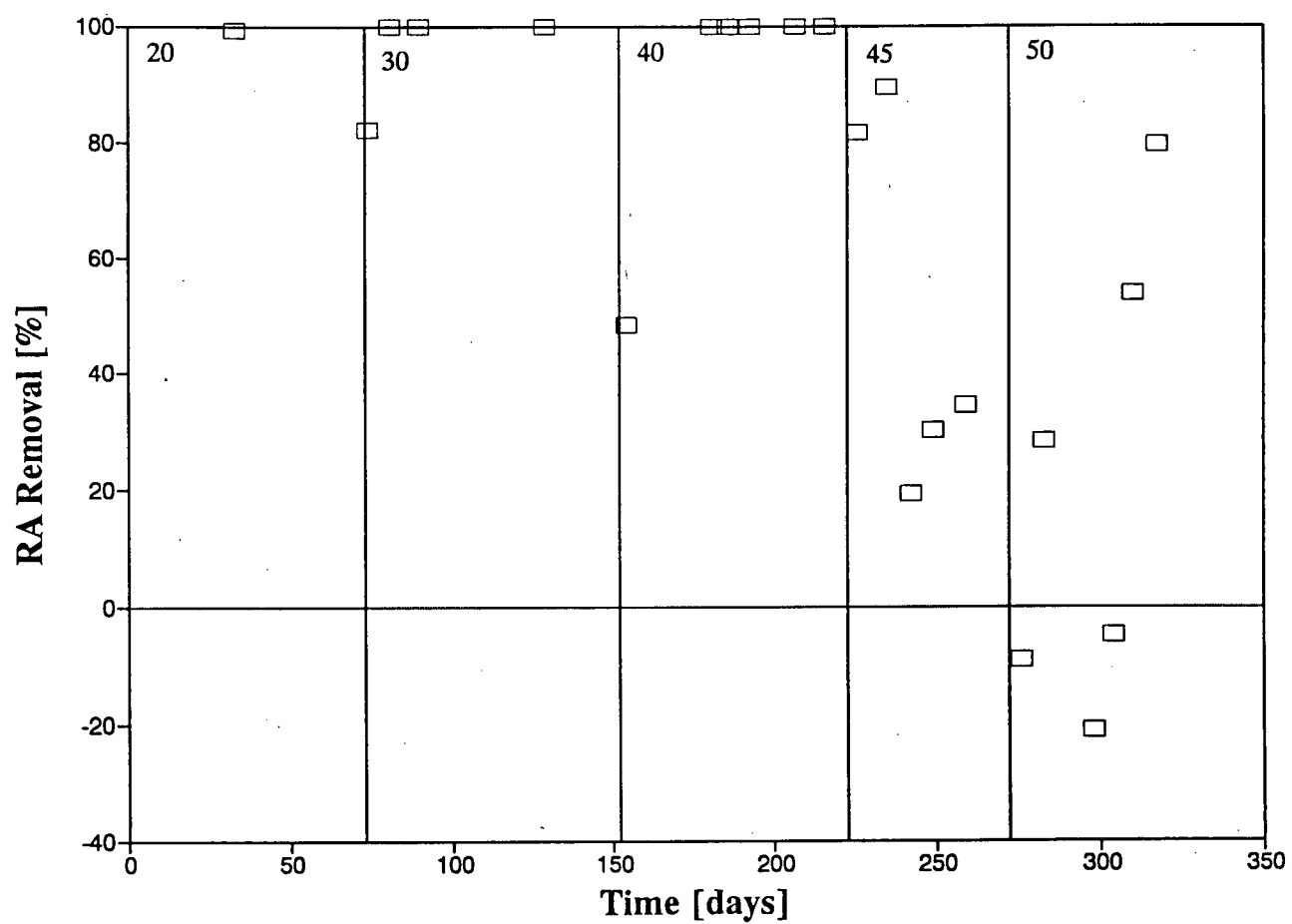


Figure 39. The removal efficiencies of the total resin acids during the experimental period.

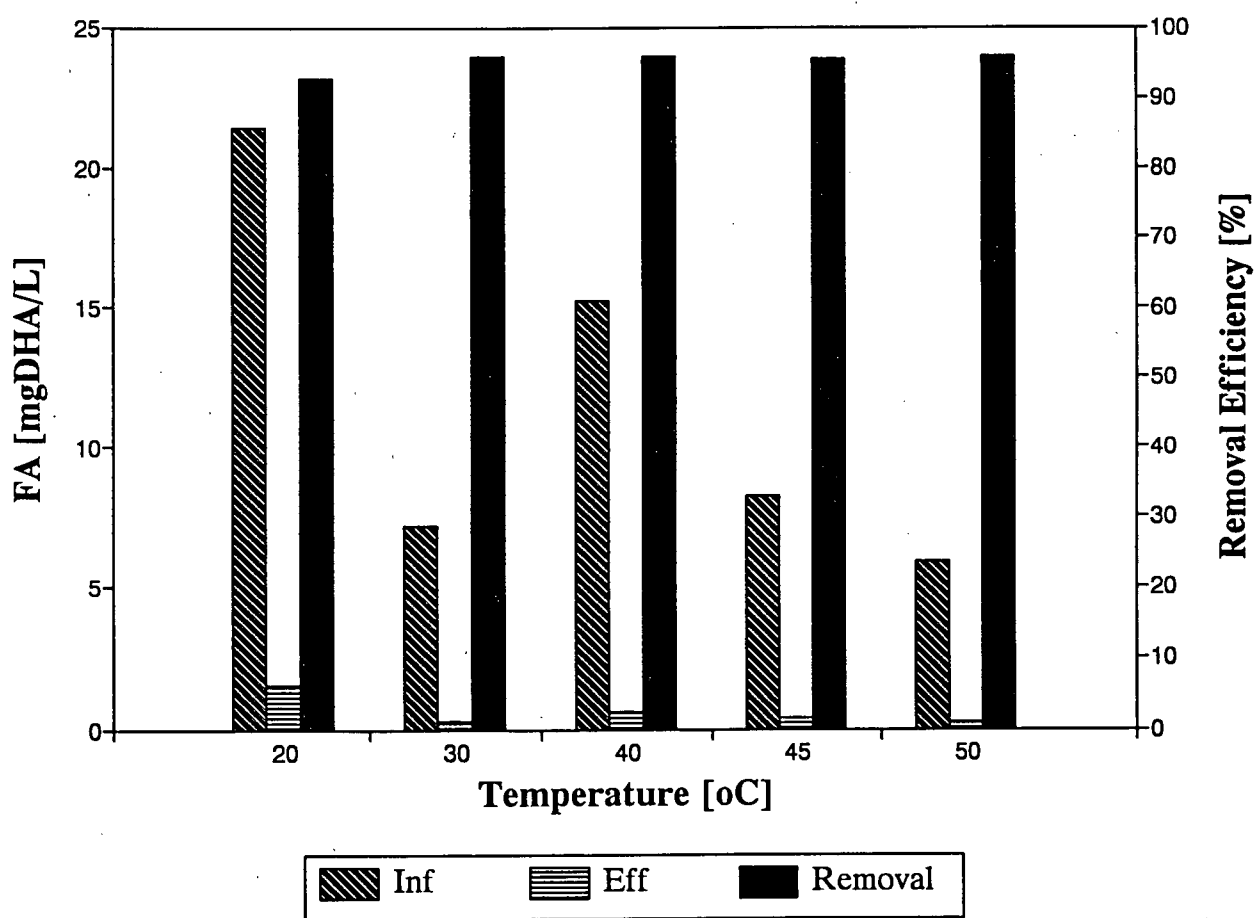


Figure 40. The average influent and effluent concentrations of fatty acids and the calculated removal efficiencies during different temperature runs.

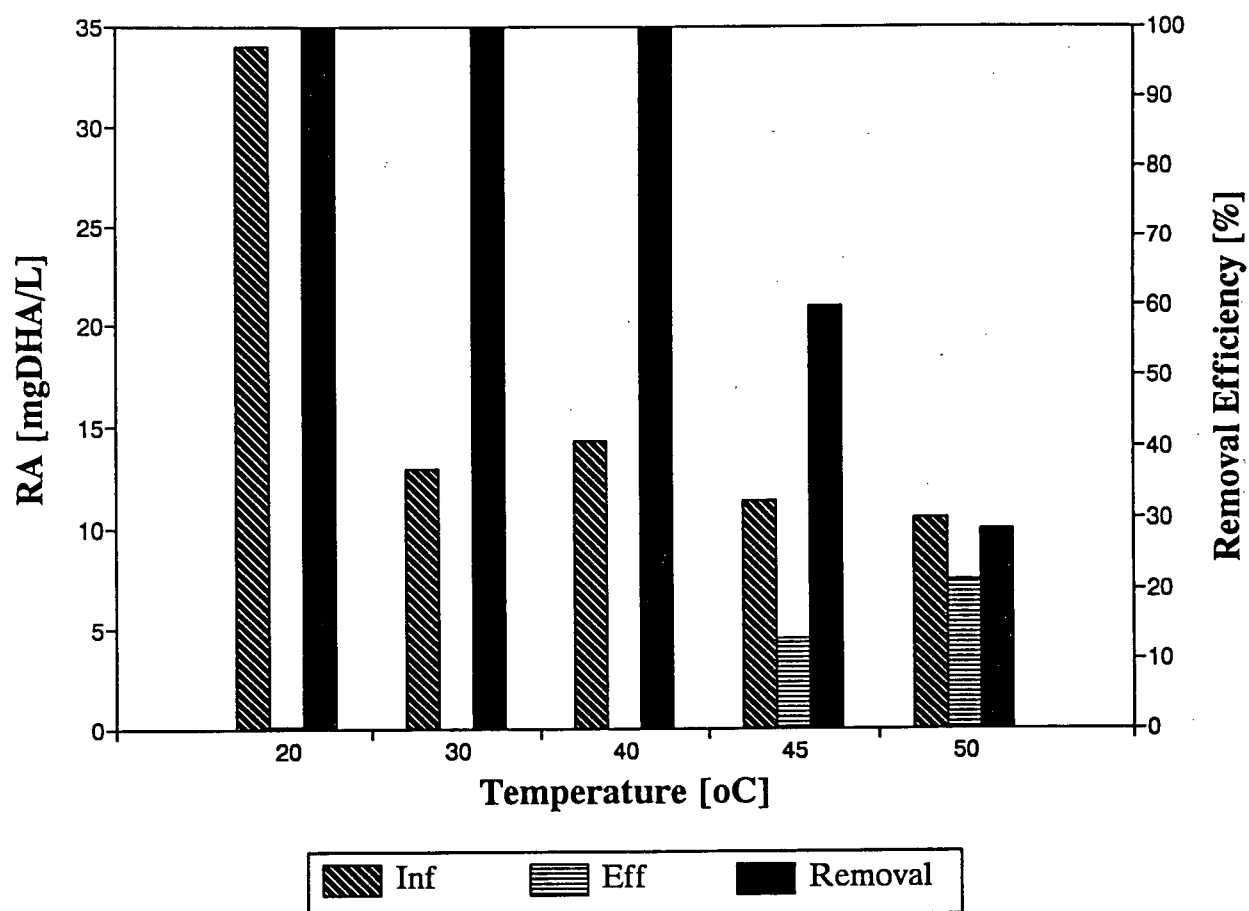


Figure 41. The average influent and effluent concentrations of resin acids and the calculated removal efficiencies during different temperature runs.

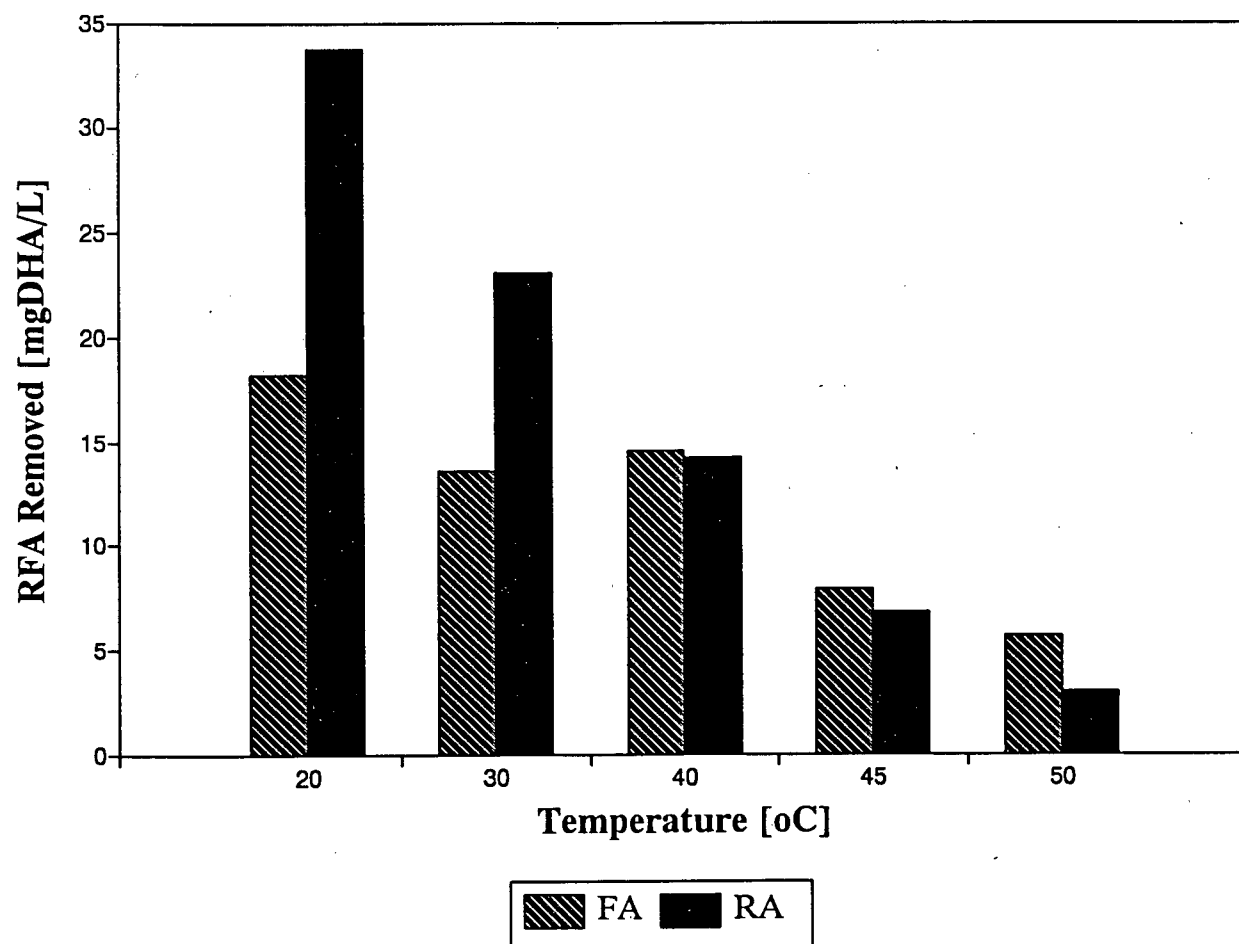


Figure 42. The resin and fatty acid mass removals during the experimental period.

#### 5.4.1.2. Resin and Fatty Acids During the React Cycle

The foregoing comparisons of the influent and the effluent examined only the inputs and outputs from the treatment system. Calculations using only the influent and effluent ignore the interaction between liquid and solid phases within the reactor and treat the reactor as a black box system. While valuable in the application of the reactor, the examination of resin and fatty acid removal during the reaction period of the reactor in the liquid and solid phases provides a better indication of the internal activity of the reactor and the extent of association of resin and fatty acids with the particulate phase. Hydrophobic organic compounds such as resin and fatty acids tend to associate with suspended organic solids (Hassett and Anderson, 1979; Landrum *et al.*, 1984; Unkulvasapaul, 1984; Morales *et al.*, 1992; Liu *et al.*, 1993; Sitholé, 1993) and thus influent resin and fatty acids added to a reactor containing large concentrations of suspended solids in the form of biomass, might tend to associate more with the solids. In addition, the resin acid levels measured during the react cycle might indicate that the efficiency of the reactor would increase if the react cycle were lengthened or shortened.

Figure 43 is a typical plot from the 30°C temperature runs for day 129. The total concentrations of both fatty acids and resin acids during the react cycle are graphed. In this graph and in similar graphs presented later, time 0 on each x-axis is just after effluent draw and influent addition were completed and aeration was begun. The react period lasted for 22.5 hours. The resin and fatty acids concentrations at the end of the previous cycle are included in the plot at -1.5 hours to give an indication of how the addition of fresh influent raises the resin and fatty acids concentrations.

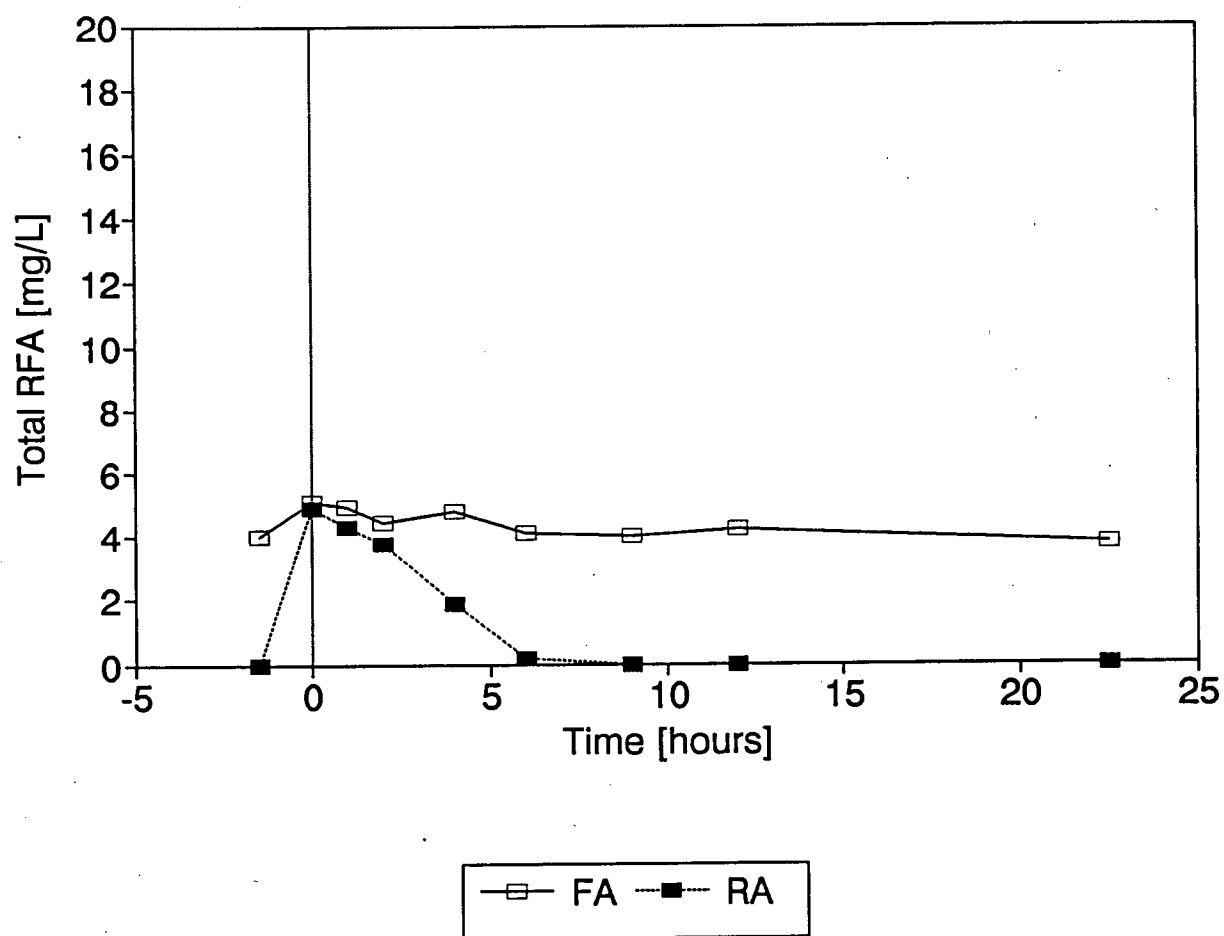


Figure 43. A typical plot from the 30°C temperature run of the mixed liquor total resin and fatty acids concentrations during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.



At time -1.5 hours, the previous react cycle was finishing and the resin and fatty acids remaining in the reactor were plotted (Figure 43). Between -1.5 hours and 0 hour, aeration was stopped and settling was allowed for one hour. Resin and fatty acids associated with the solids phase remained in the reactor in the settled solids while the resin and fatty acids associated with the liquid phase were removed in the effluent. The influent introduces new resin and fatty acids to the reactor which starts mixing at hour 0 when the react cycle begins with aeration. For the rest of the react cycle, the resin and fatty acids are monitored and their concentrations usually decrease over time.

### **Total Resin and Fatty Acids**

Figures 43, 44, 45, and 46 are four typical plots from the 30, 40, 45, and 50°C temperature runs for days 129, 216, 249, and 310 respectively. At 30°C (Figure 43), the total fatty acids added with the influent were removed completely over the react period, leaving a significant amount of fatty acids in the reactor at the end of the react cycle that were also present at the end of the previous react cycle. The resin acids, on the other hand, were removed completely long before the end of the react cycle. Thus, overall, the fatty acid concentrations during the react period were higher than the resin acid concentrations.

Similarly, at 40°C (Figure 44), resin acids were removed completely during the react period, but the time required for removal was longer at 40 than at 30°C. Similar to the pattern seen at 30°C, a significant amount of fatty acids remained in the reactor at 40°C at the end of the react period. In general, the added fatty acids tended to not start being removed until 2 to 9 hours into the react period. On all the sampling days except on day 154 which was a few days after the temperature change from 30 to 40°C, the fatty acid concentrations were significantly higher than the resin acid concentrations during the react cycle.

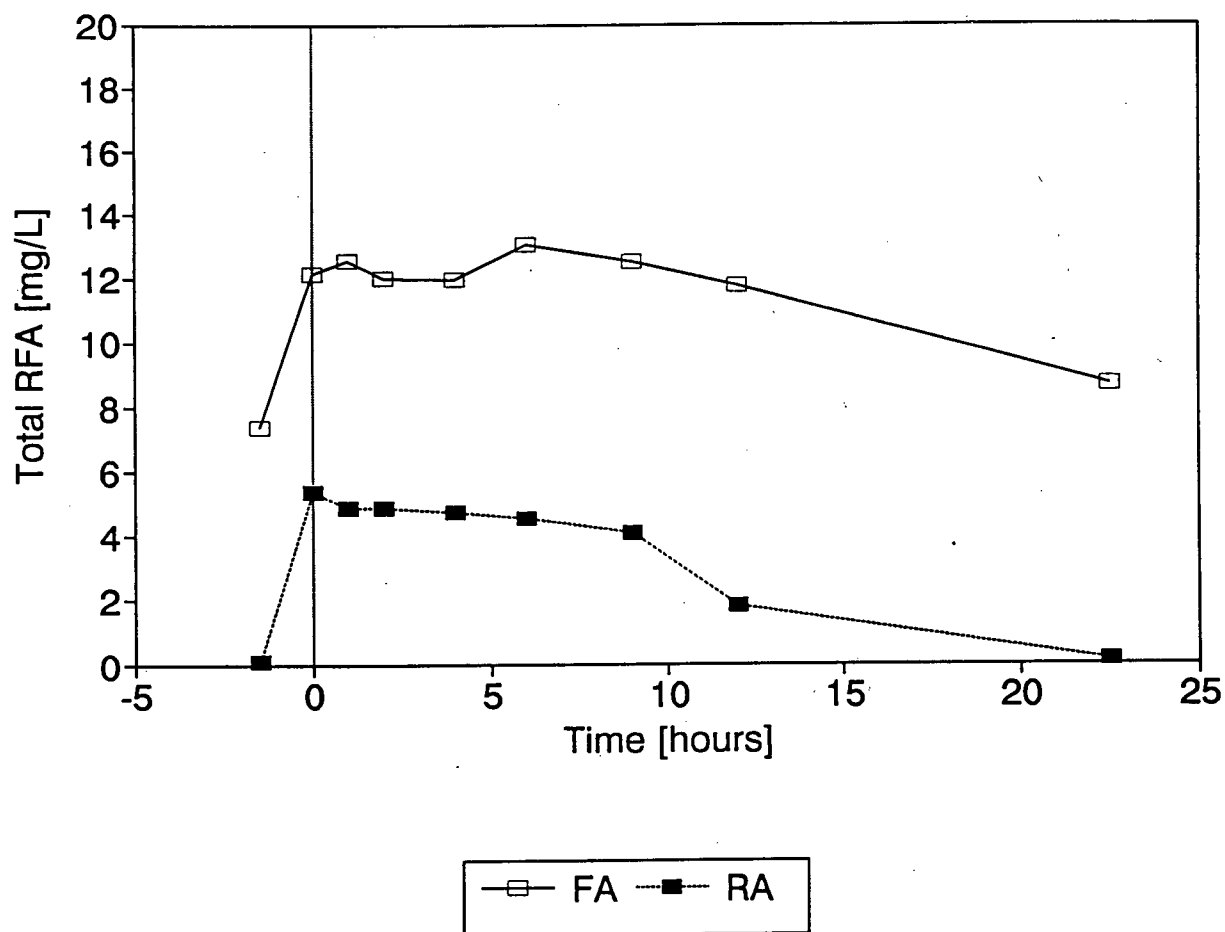


Figure 44. A typical plot from the 40°C temperature run of the mixed liquor total resin and fatty acids concentrations during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

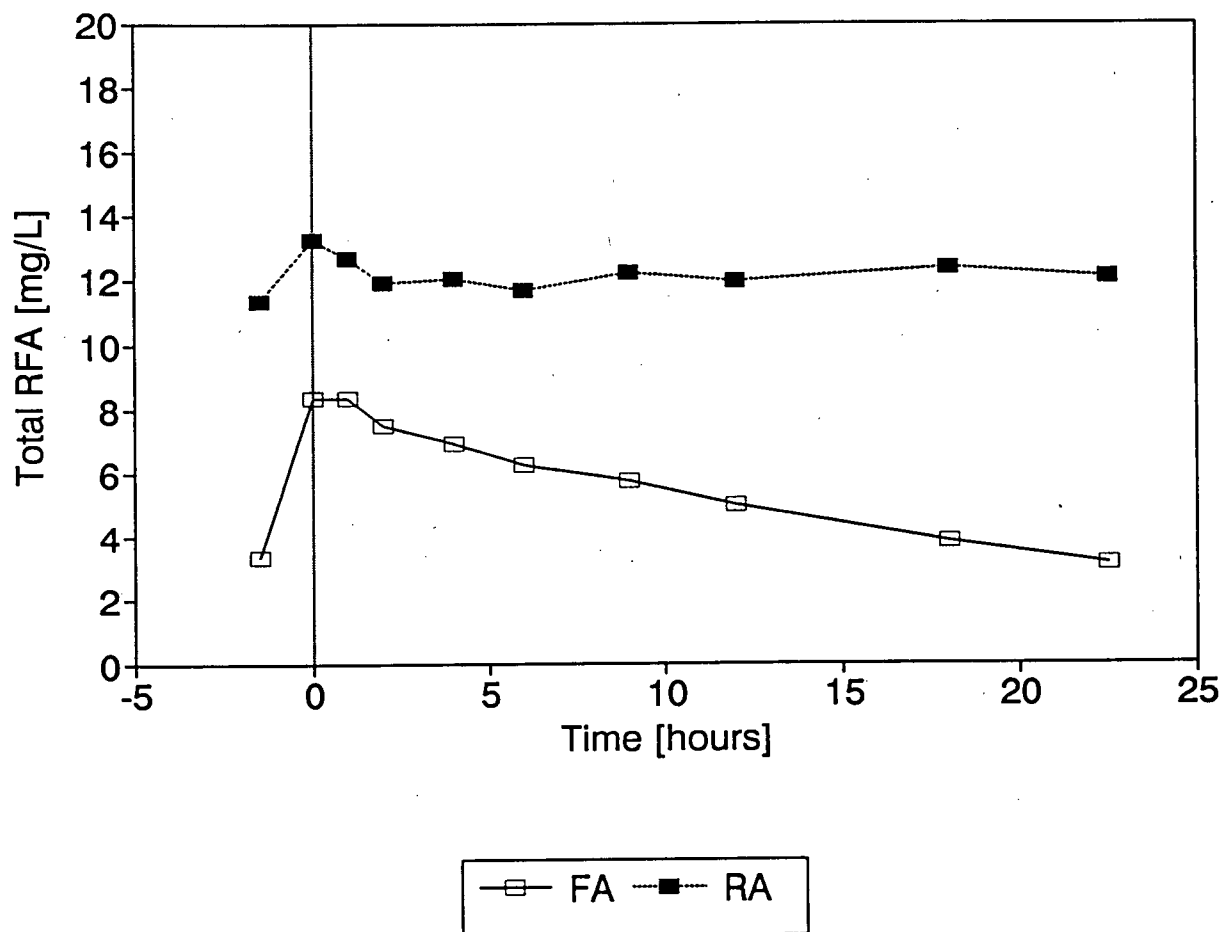


Figure 45. A typical plot from the 45°C temperature run of the mixed liquor total resin and fatty acids concentrations during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

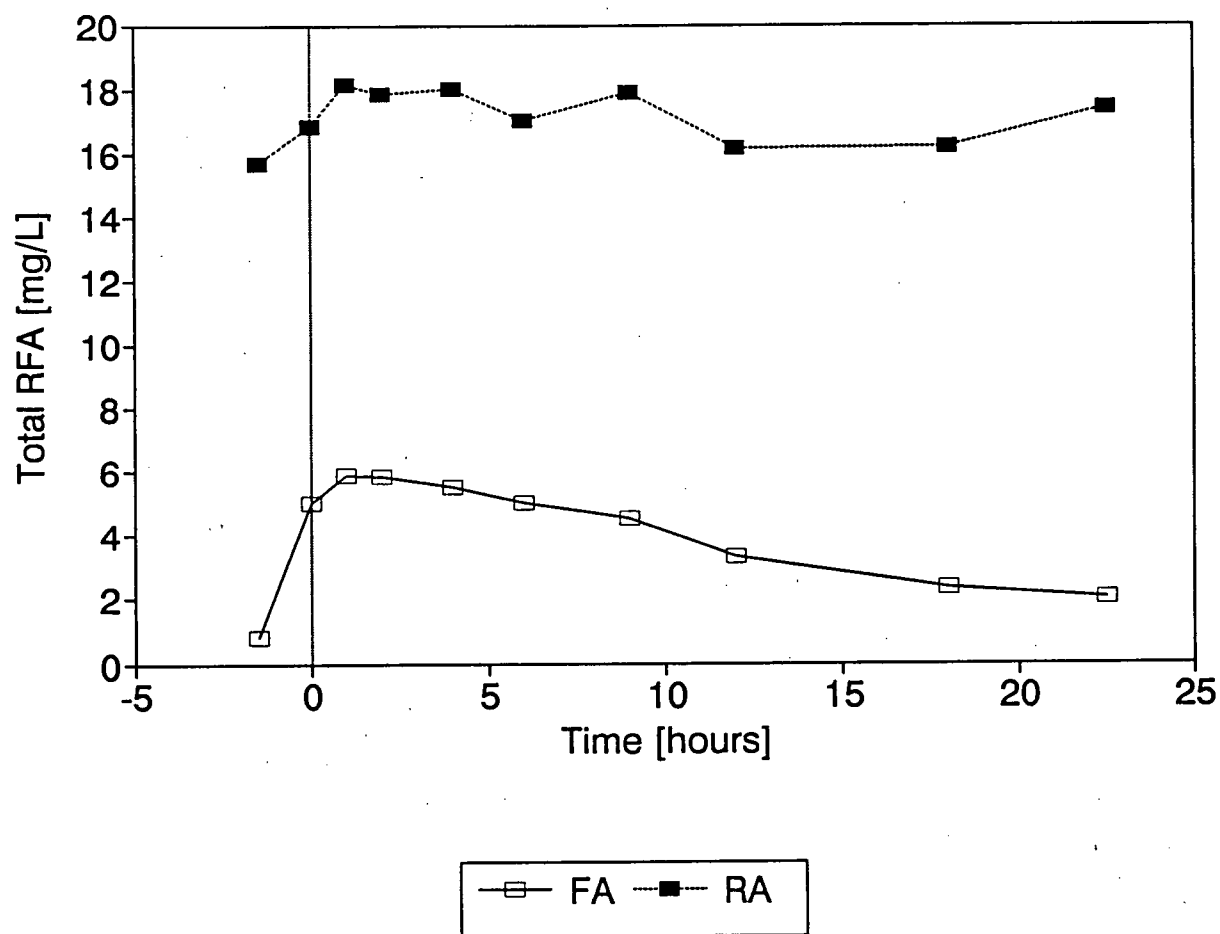


Figure 46. A typical plot from the 50°C temperature run of the mixed liquor total resin and fatty acids concentrations during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

Resin and fatty acid behaviour changed markedly at temperatures higher than 40°C. At 45°C (Figure 45) and 50°C (Figure 46), resin acid concentrations were higher than fatty acid concentrations during the react cycle instead of the inverse seen at lower temperatures. Throughout the 45°C temperature run, the resin acids were not removed completely by the end of the react cycle and appeared to accumulate, resulting in mixed liquor resin acid concentrations that were higher than the fatty acid concentrations throughout the react period (Figure 45). At 45 and 50°C (Figures 45 and 46), resin acids were not removed to any extent during the react period, in contrast to the complete removal observed at lower temperatures (Figures 43 and 44).

On the other hand, the removal of fatty acids began 1 to 2 hours into the react period and continued throughout the react period. This lag in removal was shorter than at 40°C (Figure 44). Fatty acid concentrations at the end of the react period were lower at 45 and 50°C (Figures 45 and 46) than at lower temperatures (Figures 43 and 44), but some still remained at the end of the react cycle.

Overall, resin acids were completely removed at 30 and 40°C, while at 45 and 50°C, resin acids were not significantly degraded during the react period. Resin acids were not present in the reactor at the end of the react period at 30 and 40°C, but at higher temperatures, resin acids appeared to accumulate in the reactor and were present at the end of the react period. The removal of total fatty acids continued throughout the react period at all temperatures and the concentrations remaining in the reactor at the end of the react period appeared to decrease at higher temperatures.

By looking at the RA concentrations at the end of the previous cycles, called the baseline levels, in Figures 43, 44, 45, and 46, a trend for RA accumulation in the reactor was seen. Between 40 and 45°C (Figures 44 and 45), the baseline RA level jumped from zero to

approximately 11 mg/L and further increased during the 50°C run to a concentration of about 15 mg/L. FA baseline levels, on the other hand, appeared to not increase, perhaps becoming lower as the experimental period progressed.

### **Fatty Acids in the Liquid and Solids Phases**

Figures 47, 48, 49, and 50 are taken from typical sampling days at 30, 40, 45, and 50°C respectively for fatty acids concentrations in the liquid and solids phases. At all four temperatures, the highest fatty acid concentrations during the react period are found in the solids, especially at 30, 40, and 45°C (Figures 47, 48, and 49). At 50°C (Figure 50), the fatty acid concentration in the liquid phase is lower than at lower temperatures, but this may be due to lower influent fatty acids levels (Figure 40). Most fatty acid removal occurs in the solid phase at all temperatures where the majority of the fatty acids were present. Fatty acid concentrations in the liquid phase were near zero at 30, 40, and 45°C (Figures 47, 48, and 49). At 50°C (Figure 50), however, higher fatty acid concentrations in the liquid phase allowed some removal to occur in this phase. Overall, fatty acids are mostly associated with the solids phase where most removal occurred except at 50°C where fatty acids in the liquid phase allowed some removal in the liquid phase.

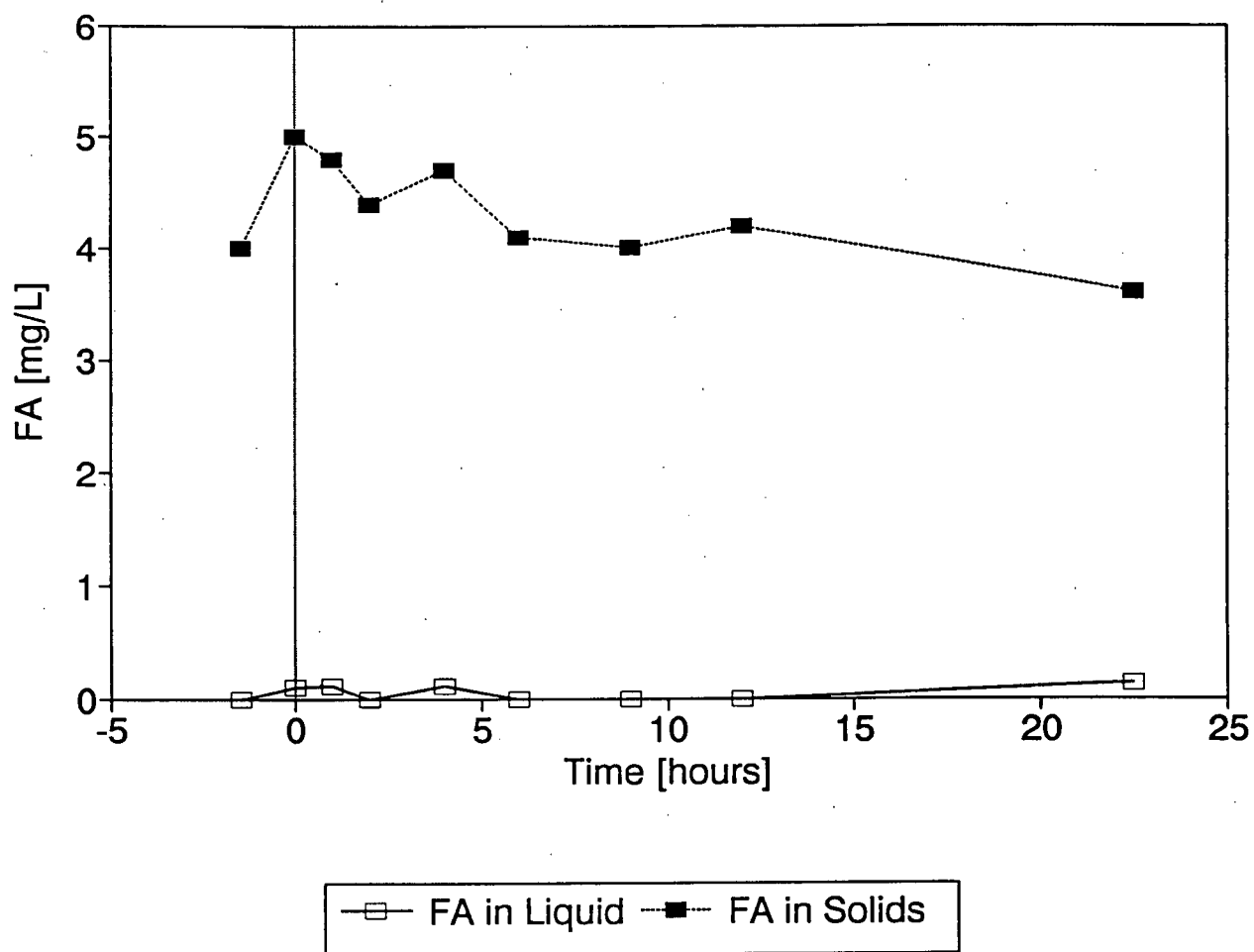


Figure 47. A typical plot from the 30°C temperature run of the fatty acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

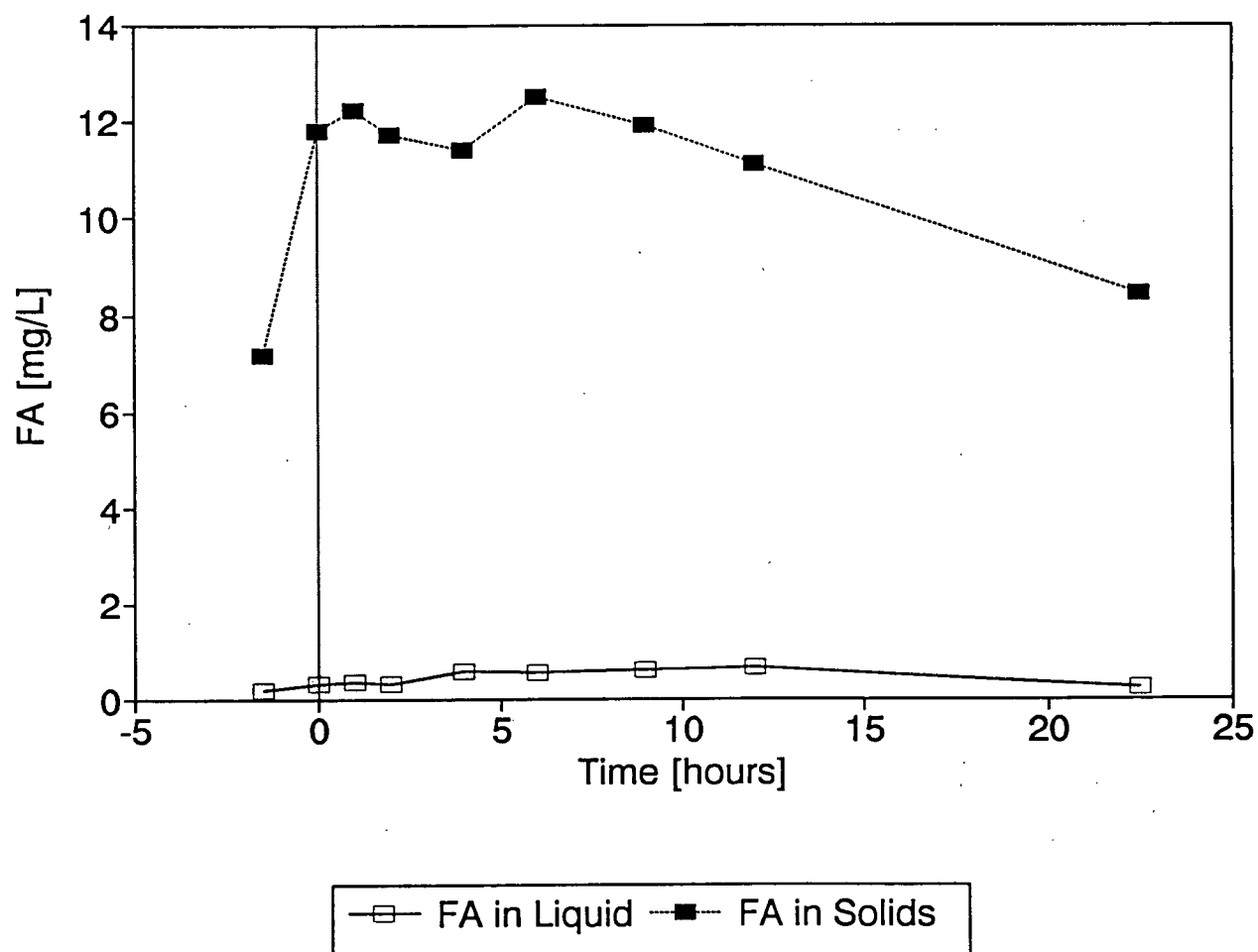


Figure 48. A typical plot from the 40°C temperature run of the fatty acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.



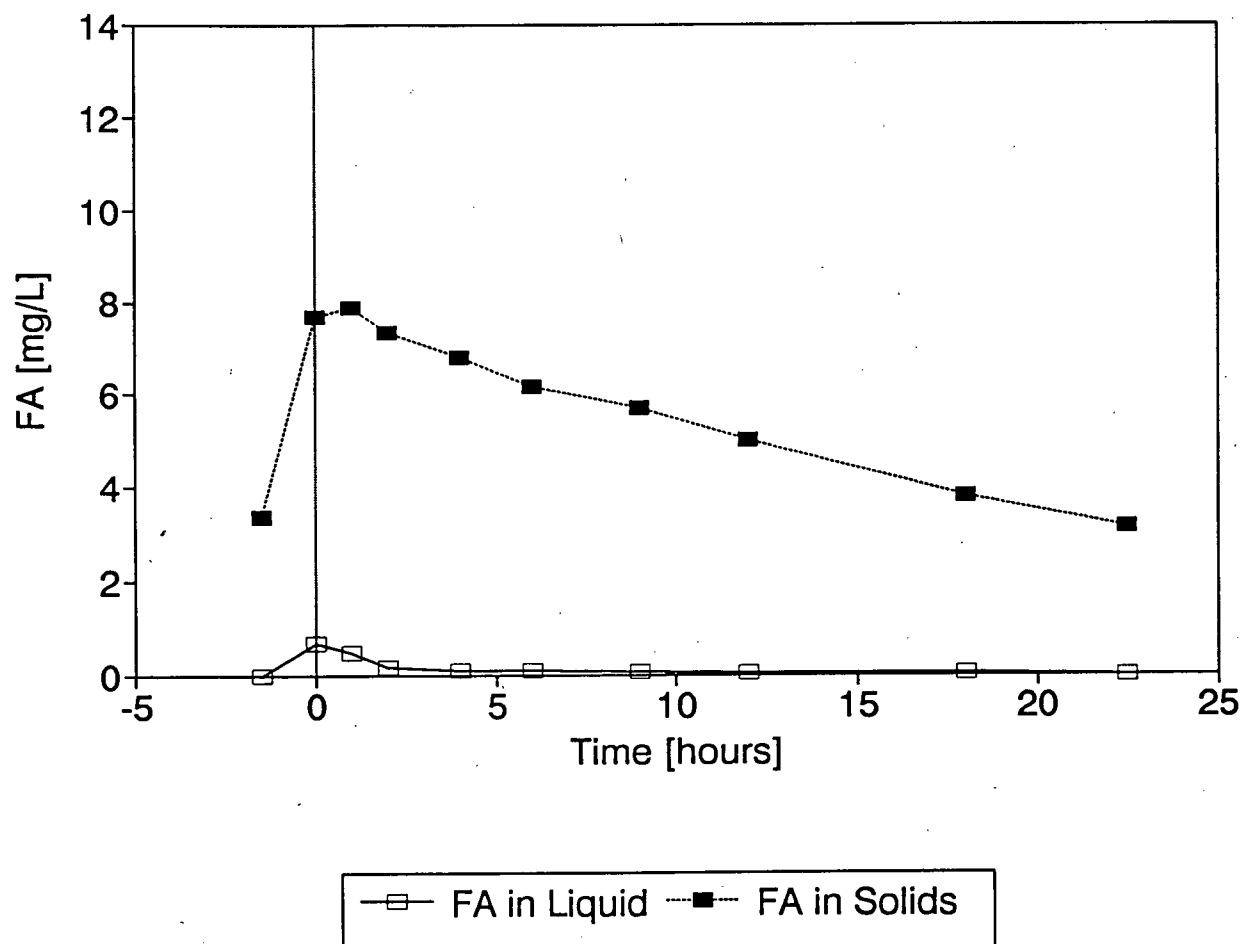


Figure 49. A typical plot from the 45°C temperature run of the fatty acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

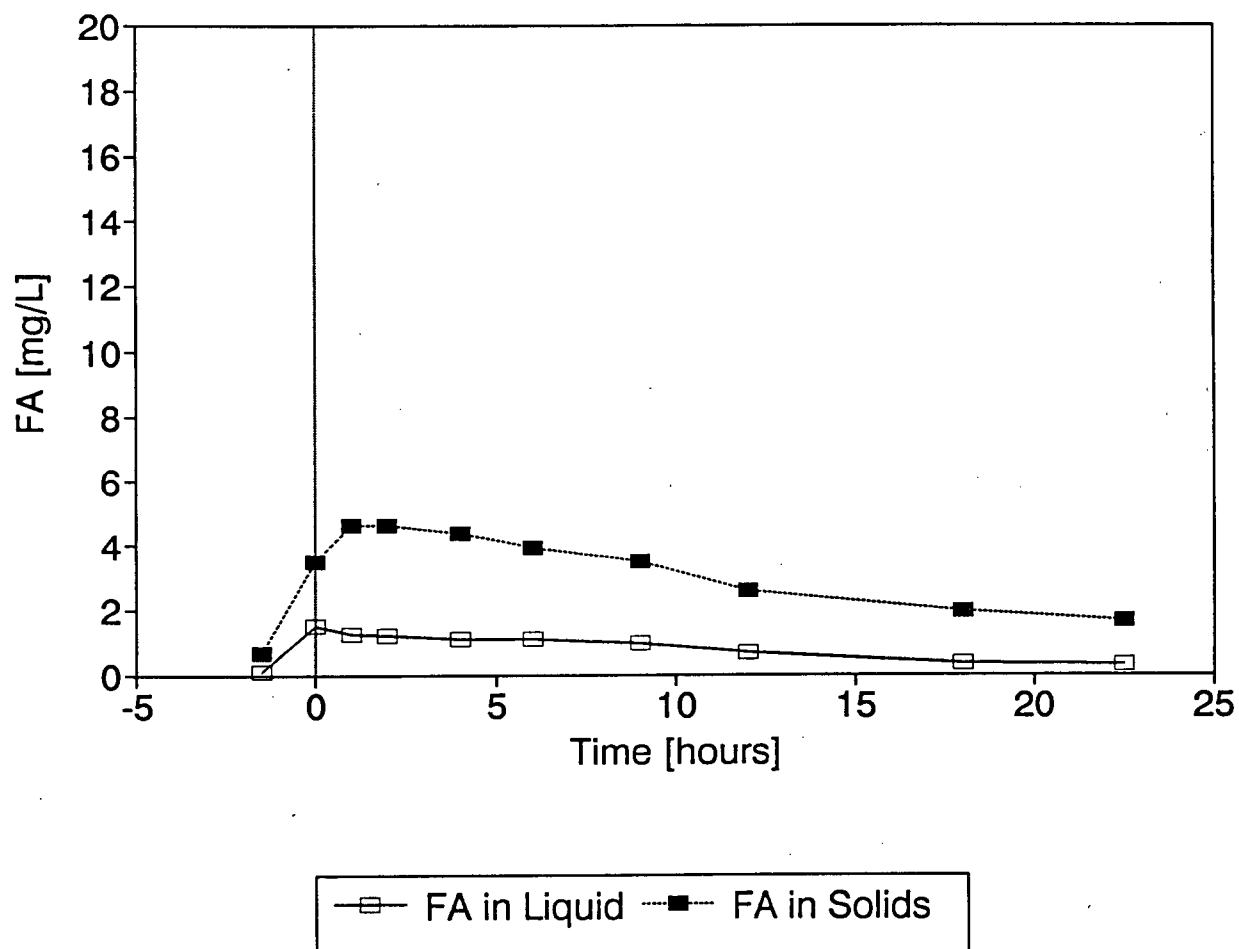


Figure 50. A typical plot from the 50°C temperature run of the fatty acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

### **Resin Acids in the Liquid and Solids Phases**

Figures 51, 52, 53, and 54 plot typical sampling days at 30, 40, 45, and 50°C respectively for resin acids concentrations in the liquid and solids phases. Generally, resin acids were most commonly found in the liquid phase, in contrast to the fatty acids which were present in the solids phase. Resin acids in both the liquid and the solids phases were completely removed at 30 and 40°C (Figures 51 and 52). At higher temperatures (Figures 53 and 54), however, a substantial amount of resin acids were present and were not removed from the two phases throughout the react period. Overall, resin acids were more associated with the liquid phase, but were present in substantial concentrations in the solids phase. At lower temperatures, where removal occurred, both phases contributed to the removal.

### **Summary**

As the treatment temperature was increased, the resin and fatty acid concentrations remaining at the end of the react cycle also increased, in agreement with the measured overall removal efficiencies discussed earlier. The fatty acids were observed to be primarily associated with the solid phase during the react cycle. The resin acids were associated with both the liquid and the solid phases, but more so with the liquid phase, during the react cycle. This explains the appearance of resin acids in the effluent at high temperatures (Figure 41), basically the liquid phase, while the fatty acids are essentially absent (Figure 40).

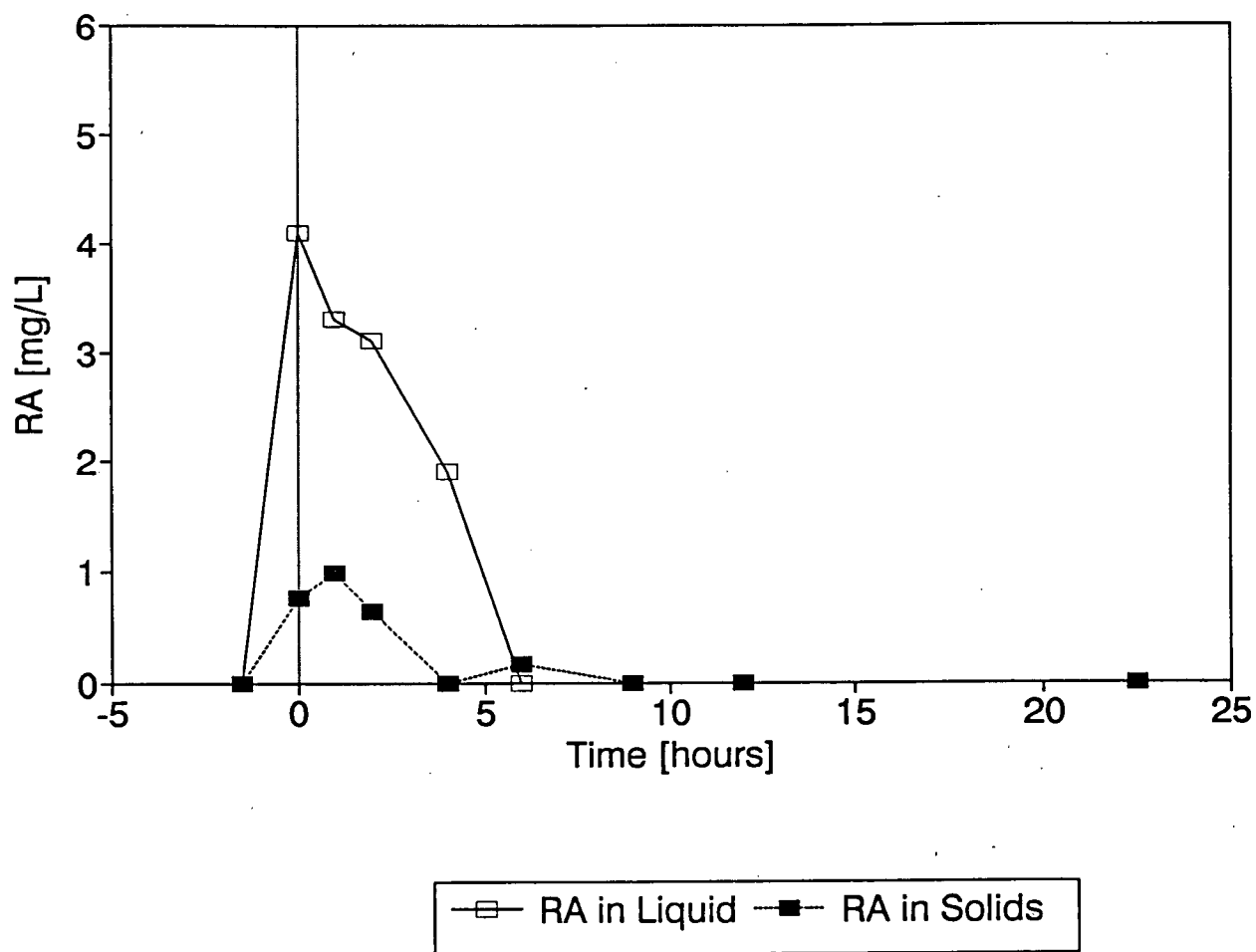


Figure 51. A typical plot from the 30°C temperature run of the resin acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

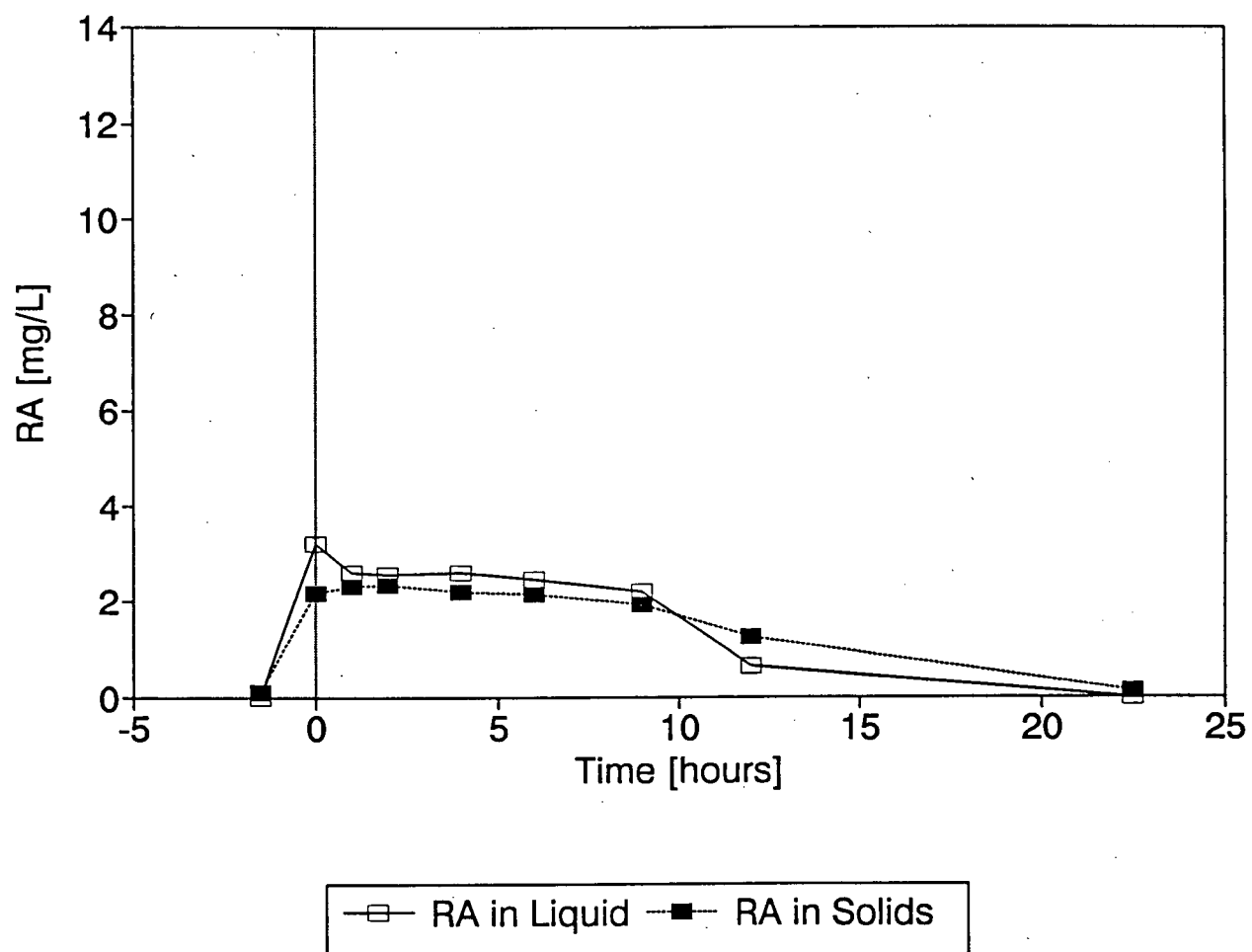


Figure 52. A typical plot from the 40°C temperature run of the resin acids concentrations in the mixed-liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

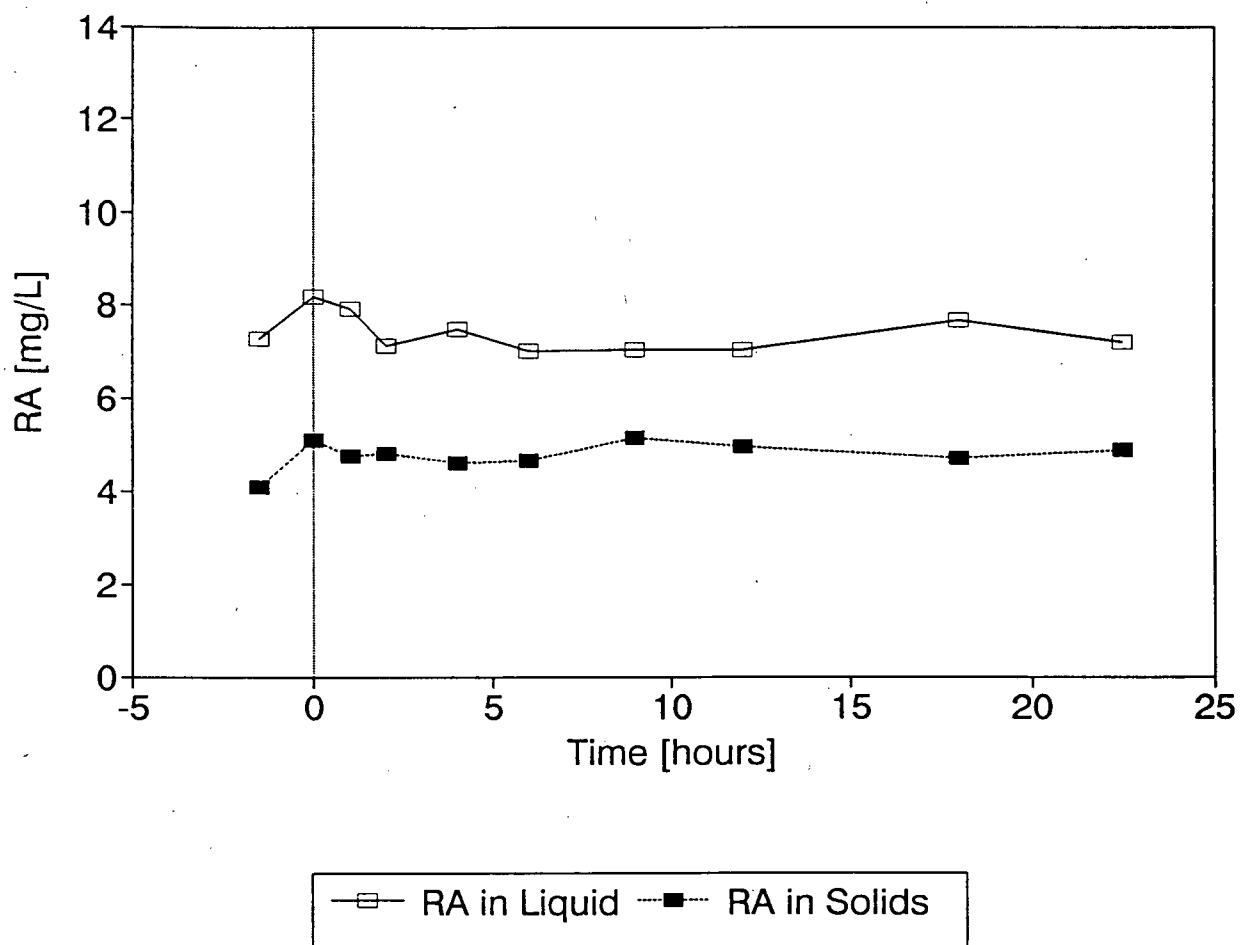


Figure 53. A typical plot from the 45°C temperature run of the resin acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

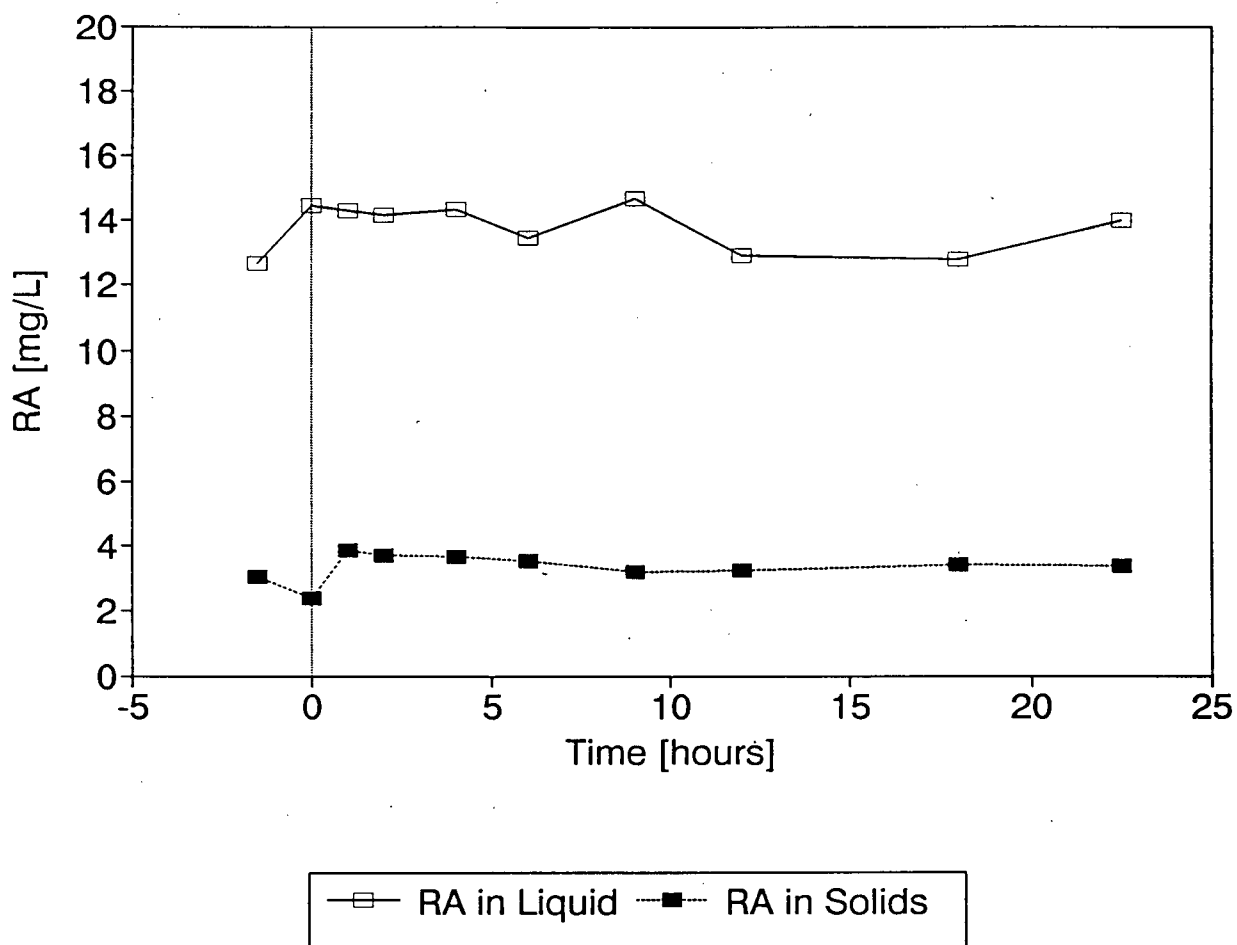


Figure 54. A typical plot from the 50°C temperature run of the resin acids concentrations in the mixed liquor liquid and solids phases during the react cycle. Time 0 on the x-axis is just after effluent and influent flows have been completed and aeration has begun.

#### 5.4.1.3. Resin and Fatty Acids Removal Rates

In an application of SBR treatment to mechanical newsprint whitewater, observed and maximum rates of resin and fatty acids removal are needed for process design. The resin and fatty acid specific removal rates were calculated in a similar manner to the specific substrate utilization rates for conventional substrates such as TDS, TOC, and COD (Equation 6) except for a few differences. Instead of the  $Q$  and  $V_r$  terms used in Equation 6, a time term,  $t$ , indicates the length of removal time (Equation 9). The length of removal time, in reality taking hours in the bioreactor, is expressed in days to maintain the same units as for the specific substrate utilization rates calculated for conventional substrates. The calculation includes a normalization to the MLVSS level in the reactor which takes account of any solids changes during the experimental period.

$$U_{RFA} = \frac{(S_o - S)}{t \cdot X} \quad \text{Eqn. 9}$$

Where	$U_{RFA}$	=	specific resin and fatty acid removal rate
	$S$	=	final concentration of substrate [g/L]
	$S_o$	=	initial concentration of substrate [g/L]
	$X$	=	concentration of mixed liquor microorganism [g MLVSS]
	$t$	=	time for RFA removal [d]

Two specific removal rates were calculated, the observed specific removal rate and the maximum specific removal rate. The observed specific removal rates utilized the removal of fatty and resin acids in the solids and liquid phases over a complete react cycle, a 22.5 hour period. Thus,  $t$  in Equation 9 was 22.5 hours in the units of days and  $S_o$  was the resin or fatty acid concentration at time 0 of the react cycle and  $S$  was the resin or fatty acid concentration



at 22.5 hours of the react cycle or at the end. Details on the individual calculations are reported in Appendix B.

The maximum specific resin and fatty acid removal rates were calculated in a similar manner to the observed specific removal rates (Equation 9) except that the removal rates were calculated during the period of greatest removal starting near the beginning of the react cycle and not over the whole react cycle time as in the observed removal rates. Plotting the substrate concentration over the time of the react cycle similar to Figure 32 and using the slope helped find the time period of fastest removal. The substrate concentrations ( $S_0$  and  $S$ ) are those seen at the beginning and at the end of this time period of maximum removal ( $t$ ). The specifics of the calculation of the maximum specific removal rate are described in Appendix B.

### **Observed Removal Rates**

Observed specific removal rates for resin and fatty acids were averaged for each temperature and plotted in Figure 55. The observed specific removal rates generally decreased with higher temperatures. The fatty acid removal rate increased from 30 to 40°C and then decreased with temperature, while the resin acid removal rates decreased with increasing temperature starting at 30°C. The resin acid removal rates decreased to a greater degree than fatty acids at 45 and 50°C. However, like removal efficiency calculations, removal rate calculations are affected by the amount of material available to be removed. The low influent fatty acid concentrations during the last two temperature runs (Figure 36) might have contributed to lower calculated rates.

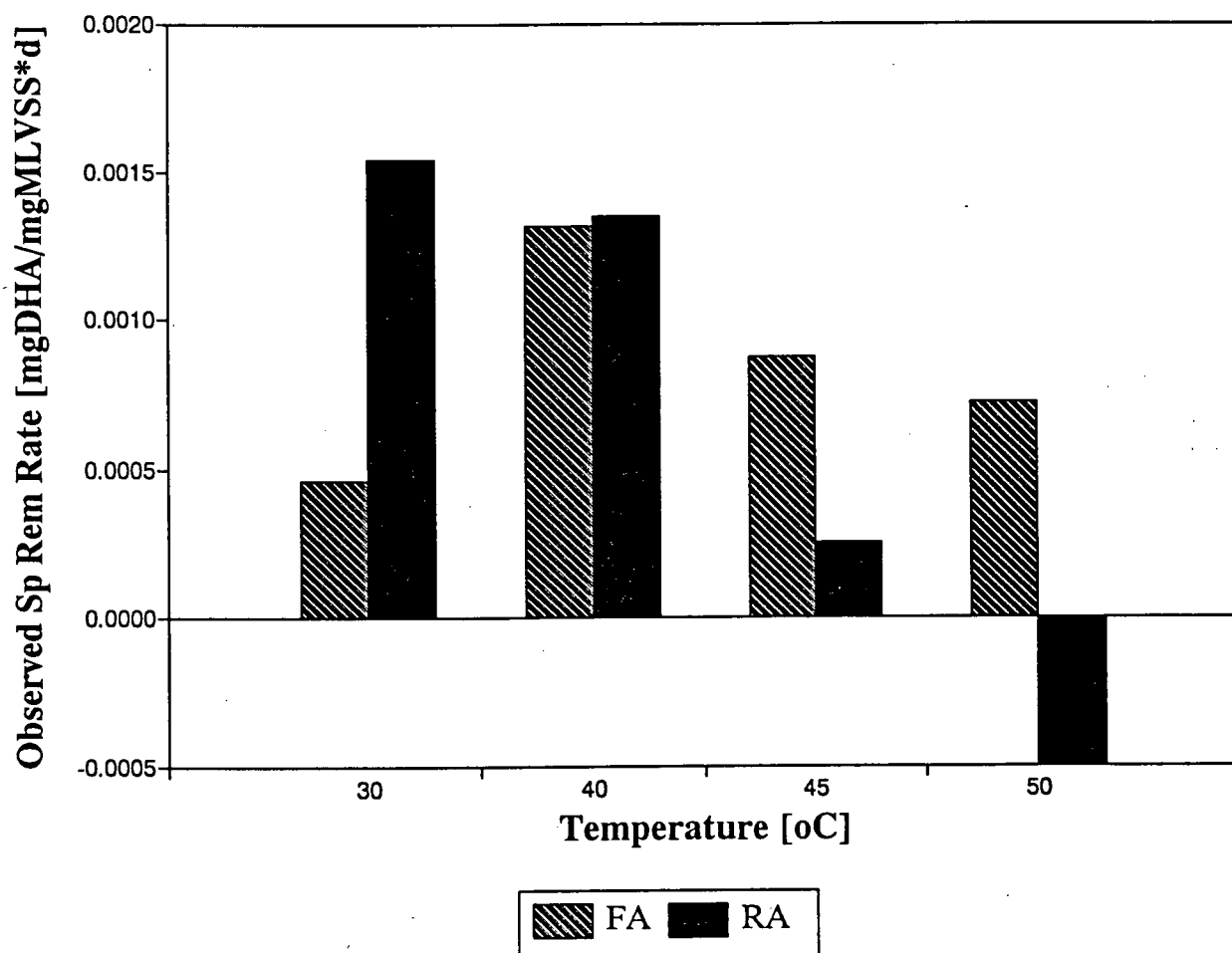


Figure 55. The observed resin and fatty acid specific removal rates during the complete react cycle, a 22.5 hour period during the different temperature runs.

### Maximum Removal Rates

While the observed resin and fatty acid specific removal rates described the particular experimental system investigated, the maximum resin and fatty acid specific removal rates help define the resin and fatty acid removal activity near the beginning of the reactor cycle when substrate is least likely to be limited. During the 22.5 hour react cycle of the reactor, resin and fatty acids could have been degraded before the end of the react period. To optimize treatment, the react time could be shortened to the period of maximum removal.

Figure 56 plots the maximum specific removal rates for fatty and resin acids during the reactor cycle. The maximum specific removal rates for fatty acids exhibited no obvious trends with temperature, but rates were higher at 40, 45 and 50°C than at 30°C. Resin acid maximum specific removal rates, on the other hand, decreased with increasing temperature. The maximum specific removal rates measure the removal rate at the beginning of the react cycle, so are not limited by low concentrations of substrate.

Figure 57 plots the observed and the maximum specific removal rates for resin and fatty acids with the same y-axis for comparison. Except at 30°C where they are equal, the maximum fatty acid specific removal rates are about twice as large as the observed removal rates. For resin acids, on the other hand, in general, the maximum removal rates are about four times higher than the observed removal rates.

Removal rates were also calculated for individual compounds such as palmitic acid. The maximum specific removal rates for individual resin and fatty acids are reported in Appendix C.

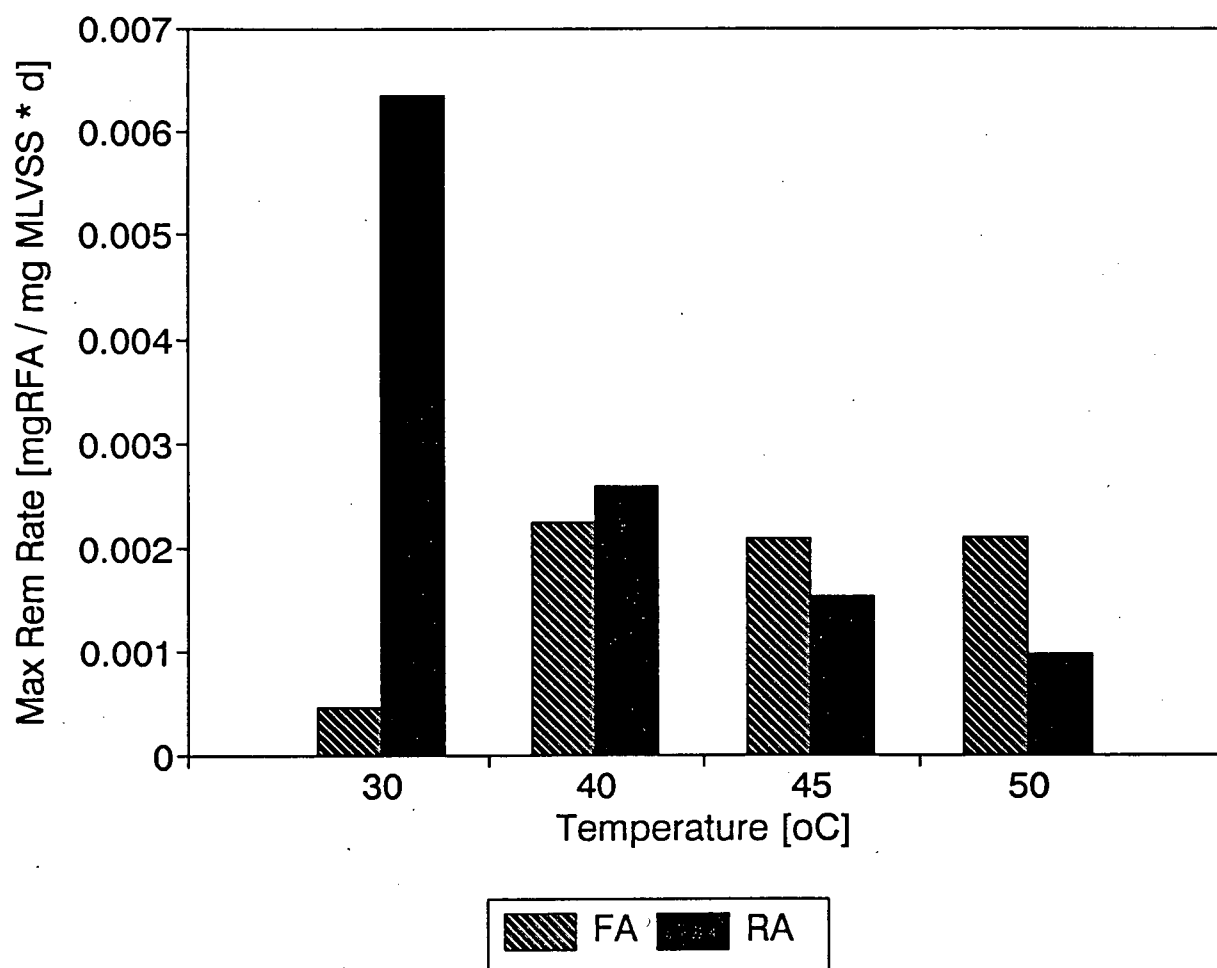


Figure 56. The maximum specific removal rates for resin and fatty acids at the beginning of the react cycle during the different temperature runs.

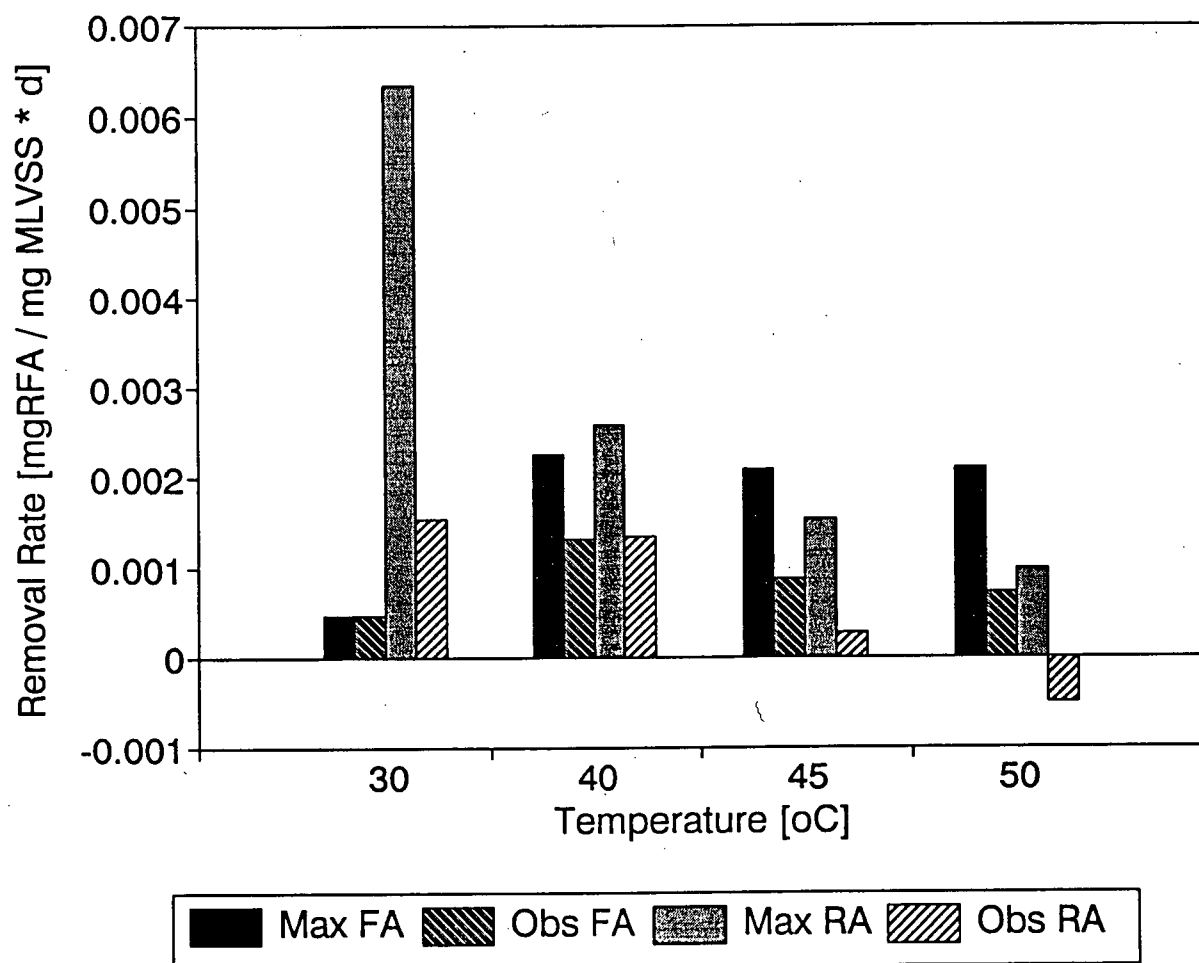


Figure 57. The observed and the maximum specific removal rates for resin and fatty acids are plotted with the same y-axis for comparison.

#### 5.4.2. Fate of the Resin and Fatty Acids

As seen in the previous sections, the resin acids were removed to varying degrees within the reactor. Removal does not necessarily mean that extensive biological degradation occurred. Possible alternative processes might have occurred, such as abiotic removal during aeration and adsorption onto the experimental apparatus.

Some removal of resin and fatty acids might have occurred through non-biological air oxidation rather than biological degradation. Theoretically, non-biological air oxidation is possible because oxygen attacks the unsaturated double bonds in the resin and fatty acid molecules (Swern, 1961; Kochhar, 1993; Liu *et al.*, 1993). Liu *et al.* (1993) studied the static air oxidation of a concentrated CTMP effluent with resin and fatty acid concentrations of 44 mg/L, to determine the non-biological component of removal. A resin and fatty acid removal of only 10% was found after 12 hour of aeration and, after 24 hours of aeration, about 12% of the original resin and fatty acid concentration was removed (Liu *et al.*, 1993). No investigation into the adsorption of resin and fatty acids onto the surfaces of the experimental apparatus was reported so these figures might include some surface adsorption. Nevertheless, the air oxidation contributed only slightly to the removal of resin and fatty acids and thus air oxidation in this whitewater treatment research was probably not a major removal mechanism.

As noted above, resin and fatty acid removal could be affected by adsorption onto the surfaces of the experimental apparatus such as the reactor walls or the effluent and aeration tubing (Figure 14). This was not considered to be a significant factor in the present study because all equipment had been exposed continuously to influent levels of resin and fatty acids during the four months acclimatization stage prior to the experimental period. Thus any surfaces exposed to the reactor contents would be saturated with adsorbed resin and fatty acids.

One alternative fate mechanism for the resin and fatty acid removal that was investigated was accumulation in the solids. Another possible fate for the resin and fatty acids that was also investigated was the transformation into compounds that differed from the 13 resin and fatty acids measured.

#### **5.4.2.1. Solids RFA Content**

One possible mechanism for removal of resin and fatty acids from the influent is their accumulation in the reactor solids (Liu *et al.*, 1993). Because reactor biomass levels fluctuated throughout the experimental period, the RFA content of the biomass solids, by mass, was used for comparison. Figures 58 and 59 plot the fatty and resin acid content of the solids, respectively. The fatty acid content of the reactor solids (Figure 58) decreased from the 40 to 45 to 50°C temperature runs. Whereas the resin acid content of the reactor solids (Figure 59) increased with increasing temperature. Even so, after operation for over 300 days, the reactor resin or fatty acid concentrations remained relatively low at up to 0.25% of the reactor biomass by weight. The changes in resin and fatty acids in the reactor were negligible compared to the sum total of influent, effluent and waste entering and exiting the reactor throughout the experimental period as seen before (Figures A5 and A6, Appendix A). Thus, although they are present at measurable concentrations in the solids, resin and fatty acids did not appear to accumulate in the reactor biomass phase throughout the experimental period.

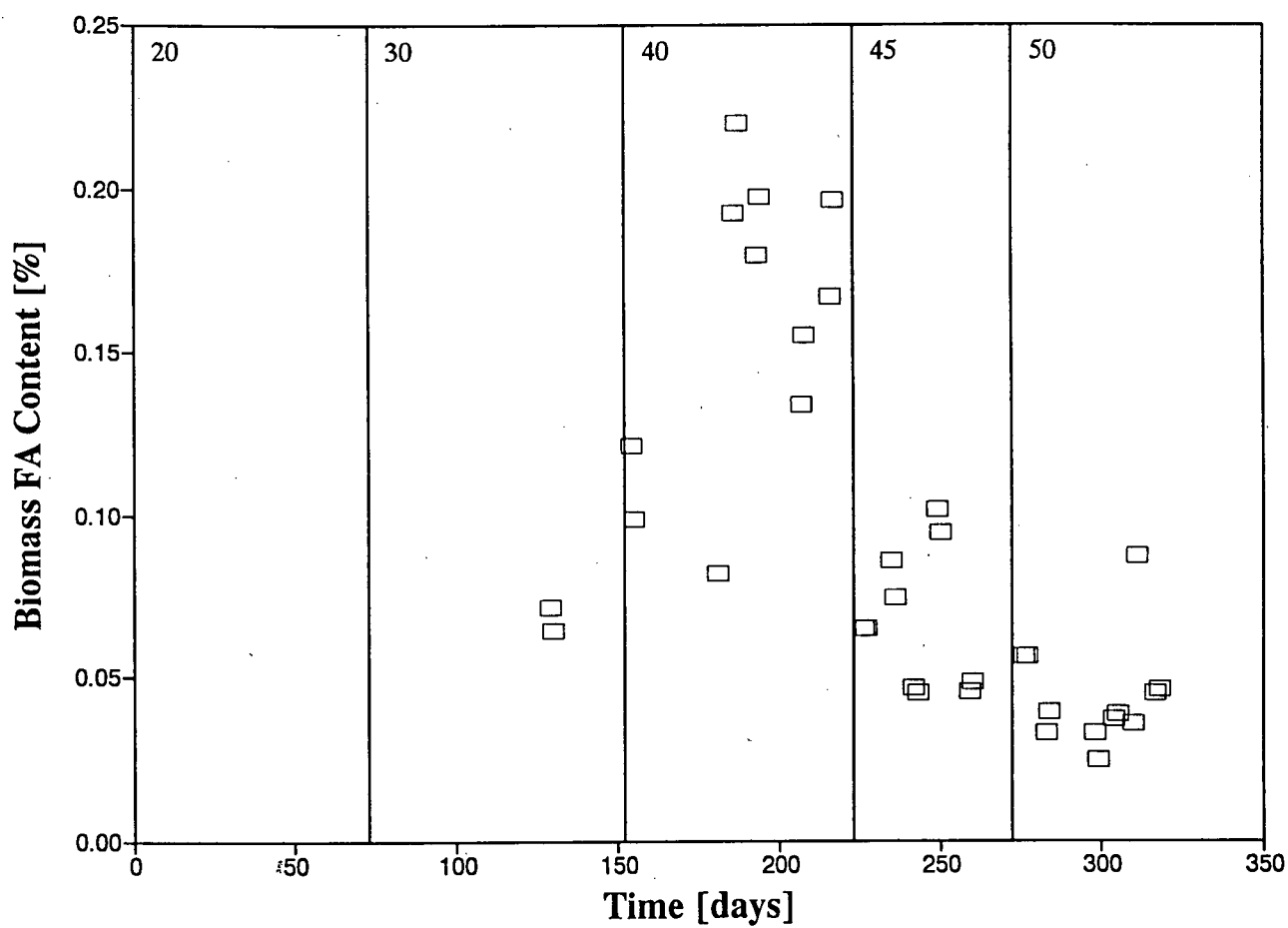


Figure 58. The biomass fatty acid content throughout the experimental period.



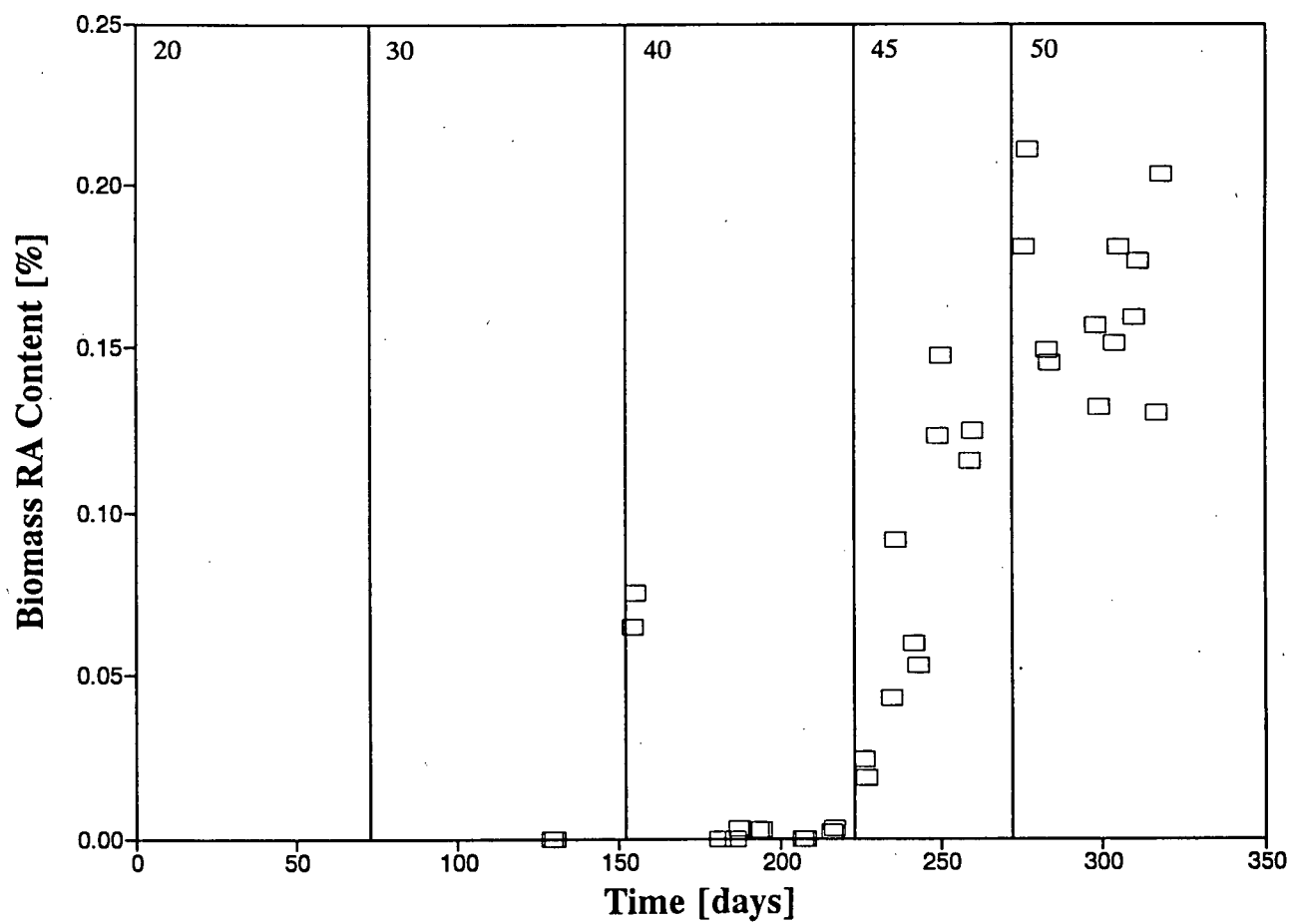


Figure 59. The biomass resin acid content throughout the experimental period.

#### 5.4.2.2. The Accumulation of Closely-Related RFA Transformation Products

If resin and fatty acids were biodegraded, they might have been only partially transformed into byproducts which might have similar properties to those of the original resin and fatty acids (Kringstad and Lindström, 1984; Ohtani *et al.*, 1986; Scott, 1989; Sitholé, 1992). Also, resin and fatty acids are just one of the identified groups of compounds of concern in closed whitewater systems (Scott, 1989). Therefore, an attempt was made to quantify the overall removal of extractable and chromatographable component, albeit unidentified, during SBR treatment.

This general measurement was made by summing GC peak areas following the extraction and derivitization in the method used to measure resin and fatty acids (see Section 4.2.4.1.e). It was recognized that some derivatives of resin and fatty acids are not detectable through chromatography (Unkulvasapaul, 1984). Furthermore, other metabolites of resin and fatty acid degradation would chromatograph at too low a retention time to be included in the peak area sum (Atlas and Bartha, 1973; Kutney *et al.*, 1981a, 1981b; Kutney *et al.*, 1982; Richardson and Bloom, 1982).

As a resin or fatty acid is degraded, the original aromatic and simple ring structures are not broken as side chains are altered (Biellmann and Wennig, 1970; Biellmann and Wennig, 1971; Biellmann *et al.*, 1973a, 1973b; Kutney *et al.*, 1981a). As for the resin and fatty acids, these initial degradation compounds might give rise to problems in the running of a papermachine because their physical properties are similar to the original resin or fatty acid (Kringstad and Lindström, 1984; Ohtani *et al.*, 1986; Scott, 1989; Sitholé, 1992). These initial degradation products may appear on the chromatograph in the vicinity of the other resin and fatty acids and thus an area summation of that part of the chromatograph might include these compounds (Atlas and Bartha, 1973; Rogers, 1973; Keith, 1976; Kutney *et al.*, 1982; Unkulvasapaul, 1984; Kutney *et al.*, 1988; McFarlane and Clark, 1988). Further degradation would break the

cyclic structures, splitting the molecule into fragments of lower molecular weight and probably would not appear in the chromatogram window for peak area summation (Biellmann and Wennig, 1970; Biellmann and Wennig, 1971; Biellmann *et al.*, 1973a, 1973b; Keith, 1976). These lower molecular weight fragments, not measured in the retention time range of the peak area summation because of their low molecular weights, could be straight chain compounds that would be more easily degraded (Keith, 1976; Richardson and Bloom, 1983).

The peak areas of all extracted compounds detected by the GC were summed for the influent and effluent for the sampling days illustrated in Figures 43, 44, 45 and 46, one for each temperature run, 30, 40, 45 and 50°C. A large distinct peak, called peak A, present in all influent samples and most effluent samples marked the beginning of the region over which peak areas were summed. Peak A occurred before the palmitic acid peak (Figure 60), detected at between 14.733 and 15.120 minutes using the temperature program detailed in Table 10. The peak area summation ended at methyl tricosanoate and did not include the peaks of the added compounds used in QA/QC such as o-methylpodocarpic acid, methyl heneicosanoate and tricosanoic acid.

On different sampling days and for different samples, the chromatography response was different. So, in order to compare peak area summations with each other, they were normalized. The peak areas in all the influent and effluent samples of methyl heneicosanoate, an internal standard added to all samples in a known amount, were averaged. The areas of the individual chromatographs were normalized by using the ratio between the calculated average methyl heneicosanoate value and the methyl heneicosanoate peak areas of the individual chromatographs as normalization conversion factors.

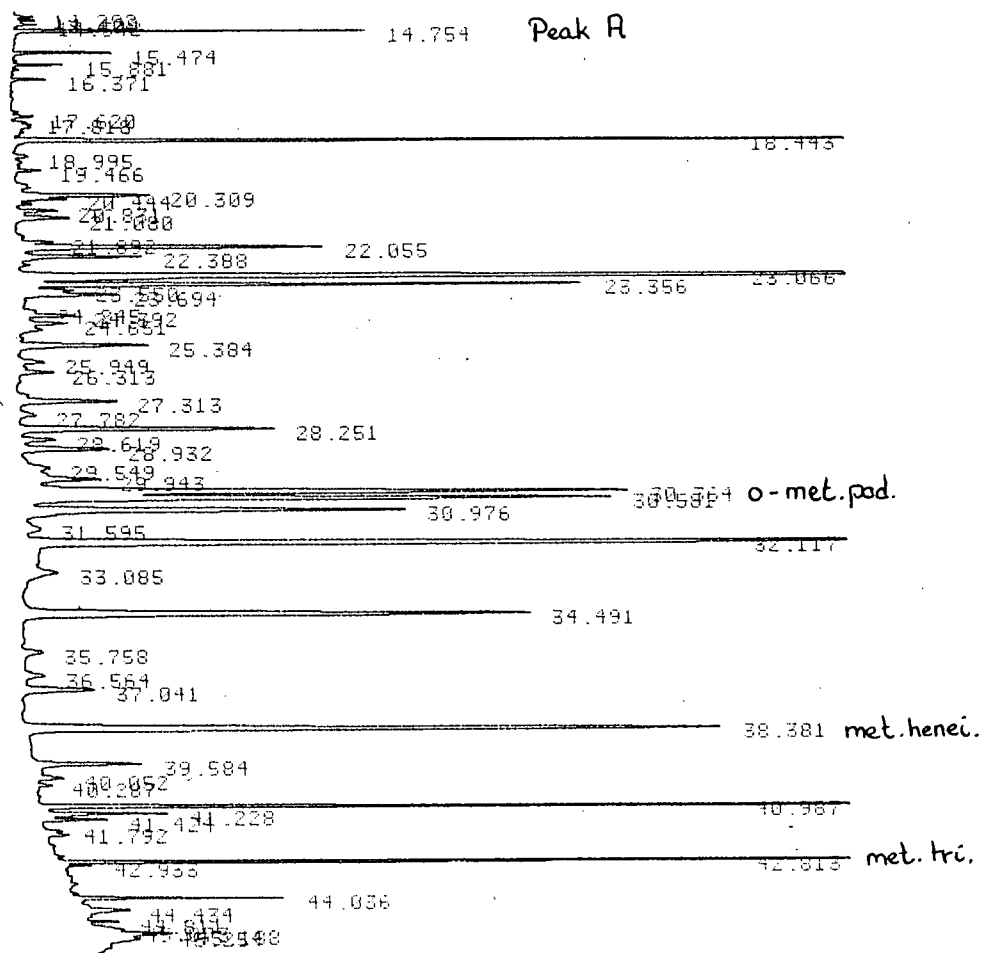


Figure 60. A typical influent chromatograph showing peak A, o-methylpodocarpic acid, methyl heneicosanoate, and methyl tricosanoate.

Figure 61 shows total peak summations of the influent and effluent at different temperature runs. Influent and effluent total peak areas were plotted for comparison. In general, resin acids accounted for a significant portion of the total peak area in both influents and effluents. All the same, material not identified as resin and fatty acids was not produced during treatment. Thus, although the reactor was effective for the removal of resin and fatty acids, closely-related transformation products did not seem to accumulate in significant quantities.

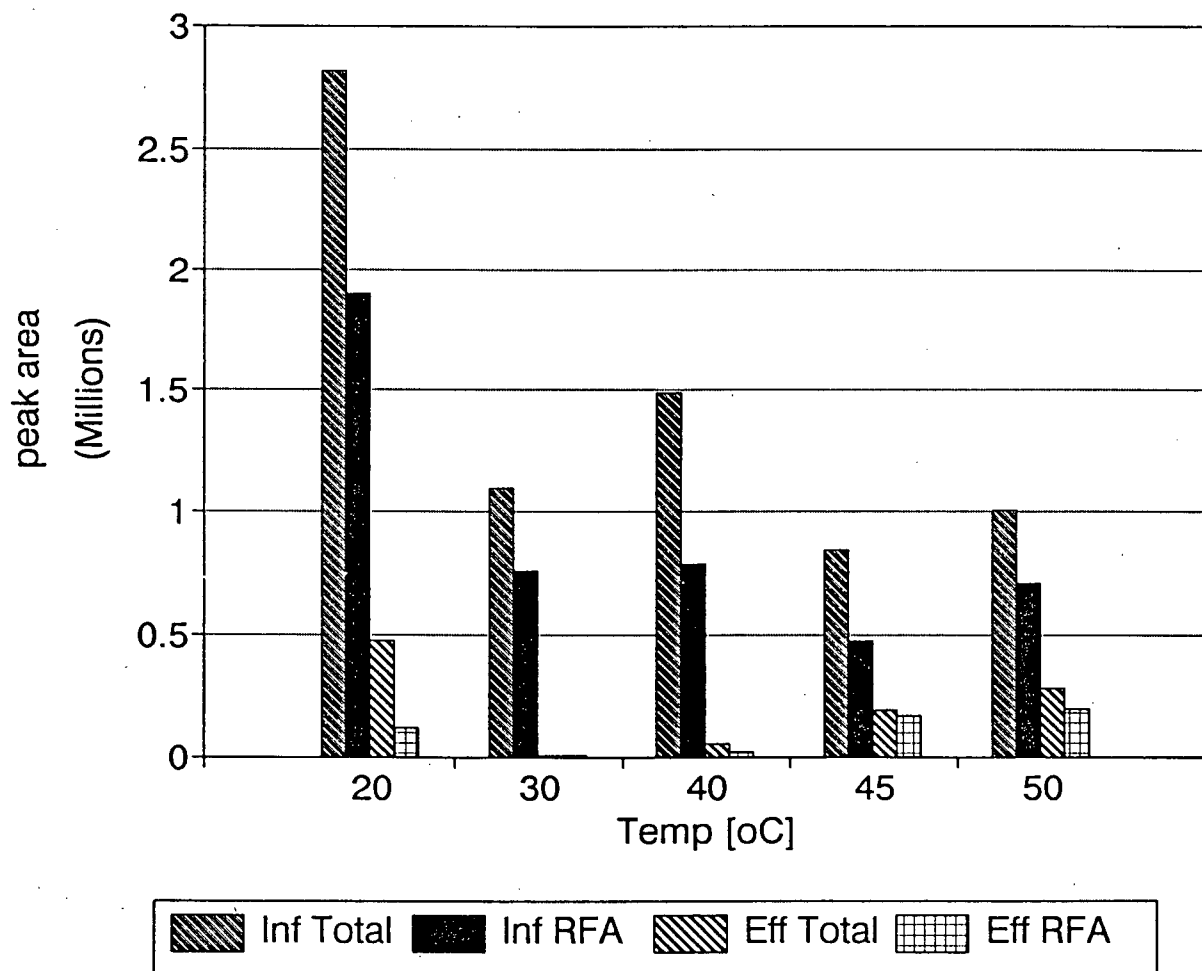


Figure 61. The total peak summation of the influent and effluent at different temperature runs. Influent and effluent total peak areas were plotted for comparison.

## 6. CONCLUSIONS AND RECOMMENDATIONS

### 6.1. Conclusions

This research investigated the treatability of a synthetic closed-system whitewater with an aerobic biological sequencing batch reactor, focusing on the removal of resin and fatty acids.

From this research, the following conclusions were made:

- (1) Based on the results obtained from this research, the biological stage of a biological membrane reactor would exhibit restricted operational viability in the treatment of a simulated whitewater for an integrated newsprint mill at high temperatures.
  - (a) A viable biomass was easily maintained at temperatures up to 40°C. Above this temperature, the maintenance of a viable biomass was difficult due to low biomass growth.
  - (b) Incomplete sludge settling contributed to the loss of biomass from the reactor
  - (c) Design parameters and performance indicators such as the food to microorganism ratio, the specific substrate utilization rate, and the growth yield were comparable to other reported values in the literature, indicating that the treatment was occurring within reasonable limits and that the deterioration in performance at high temperatures was caused primarily by excessive biomass loss.
- (2) The removal of conventional contaminants such as TDS, TOC, and COD was significant at temperatures up to and including 40°C while at higher temperatures, contaminant removal was reduced. Parameters describing reactor performance such as the specific substrate utilization rate and growth yield indicated reduced conventional contaminant removal potential at temperatures higher than 40°C.

(3)

- (a) The removal efficiencies of FA were over 95% for all temperatures, but for RA, near-complete removal was observed only up to 40°C. At higher temperatures, the removal efficiencies of RA were reduced, but still significant.
- (b) During the react cycle, FA were mainly associated with the mixed liquor solids, while RA were primarily associated with the both liquid phase and the solid phase.
- (c) Observed specific removal rates decreased with increasing temperature, while maximum specific removal rates were high for all temperatures studied. For FA, the maximum removal rates were about twice the observed removal rates, while for RA, the maximum removal rates were about four times the observed removal rates.

(4) The resin and fatty acids appeared to degrade in the biological system through means other than aerobic chemical oxidation, surface adsorption, accumulation in the biomass, and accumulation of closely-related transformation products, most likely by biological degradation.

- (a) Literature reports indicate an approximate 10% removal of RFAs through aerobic chemical oxidation under similar circumstances.
- (b) Since the reactor was operated for four months prior to the experimental period with the same equipment, surface adsorption on the apparatus, although not measured, was not expected to be significant.
- (c) The FA content in the biomass appeared to decrease with increasing temperature, while the RA content appeared to increase. The RFAs removed were not accumulated in the solid phase because the RFA content of the biomass was negligible compared to the overall mass flow through the system.



- (d) A large non-RFA extractable chromatographable component of material was removed at all temperatures, though less removal was observed at 50°C.

## **6.2. Recommendations**

- (1) By combining the aerobic biological stage with the ultrafiltration component of a biological membrane reactor, the biomass would be contained within the treatment system, so low sludge growth at high temperatures would be adequate to maintain a viable biomass and sludge settleability would not be a factor. A membrane system would necessitate constant flow conditions. In a mill application, several SBRs operating in parallel at staggered treatment stages could provide constant flow conditions. Investigation into other aerobic treatment strategies that provide a constant effluent flow such as activated sludge could be useful to a mill application. Bench-scale research is needed to assess the performance of the bioreactor combined with an ultrafiltration unit. The application of the bioreactor membrane device to a mill situation should be investigated through computer modeling and mill trials.
- (2) If the biological treatment is conducted at elevated temperatures, attention should be paid to the maintenance of conventional contaminant removal so that accumulation of these materials does not occur in the whitewater system in an application to a mill situation.
- (3) The result from this study can help control and optimize the removal of RFAs.
  - (a) If the biological treatment is conducted at elevated temperatures, attention should be paid to the removal of resin acids so that their accumulation does not occur in the whitewater system in an application to a mill situation. In

addition, the removal of other problem compounds or compound groups such as anionic trash would add insight into the usefulness of this technology.

- (b) The use of a membrane would retain the solids within the reactor to a greater degree, most likely also retaining the resin and fatty acids associated with them.
  - (c) The observed specific removal rates can be used as guidelines to shorten treatment times in a scale-up situation.
- (4) Since biological degradation seems to be the fate of most of the RFAs, care must be taken to promote rather than inhibit biological growth. In a mill application, additives and process changes should be monitored and tested to ensure they do not affect the biosystem adversely.
- (5) Biological treatment under these conditions is optimum up to 40°C and, in combination with an ultrafiltration membrane that retains contaminants and solids, temperatures higher than 40°C would probably be feasible.

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## **APPENDICES**

- APPENDIX A:** Details on the Calculation of Growth Yield
- APPENDIX B:** Details on the Calculation of RFA Removal Rates  
Observed Specific Removal Rates  
Maximum Specific Removal Rates
- APPENDIX C:** Individual RFA Removal Rates
- APPENDIX D:** Raw Experimental Data

## APPENDIX A: Details on the Calculation of Growth Yield

As part of the growth yield calculations (Table 26), total cumulative substrate removals were used. These were determined by cumulative mass balances of the substrate in the influent, effluent and wasted mixed liquor, calculated in a similar manner to VSS accumulation detailed earlier (Equation 1). In applying this calculation to substrate removal, the reactor term was negligible and outflow terms did not include the reactor biomass solids because the focus of the calculation was on the substrate removal capacities and not on sludge generation. The total substrate removed was calculated by subtracting the cumulative outflow of substrate from the cumulative input of substrate (Equation A1).

$$\text{Tot S Removed} = \text{Cum Inf S} - \text{Cum Eff S} - \text{Cum Waste S} \quad \text{Eqn. A1}$$

The TDS, TOC, DCOD, and TCOD in the waste mixed liquor were not measured directly, but were assumed to be equal to the effluent concentrations. In assuming this, the total TCOD removed might have been underestimated from time to time depending on the amount of solids in the effluent included in the TCOD concentration when it was used as the waste mixed liquor concentration. The cumulative TDS (Figure A1), TOC (Figure A2), TCOD (Figure A3), and DCOD (Figure A4) levels in the influent, effluent and wastage and the net substrate removed were calculated. The cumulative FA (Figure A5) and RA (Figure A6) levels in the influent, effluent, waste and the net substrate removal were calculated also.

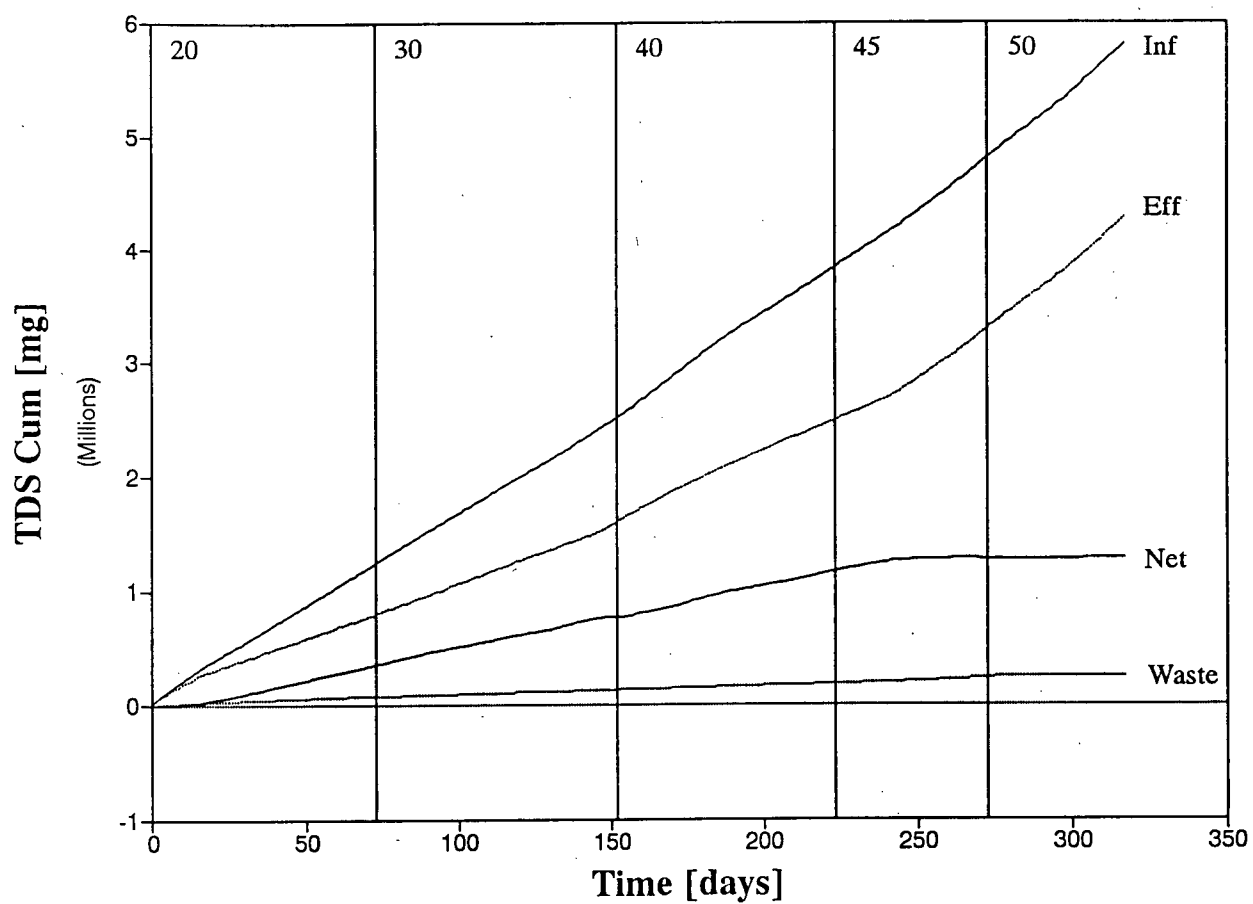


Figure A1. The cumulative TDS levels in the influent, effluent and wastage and the TDS removal during the experimental period.

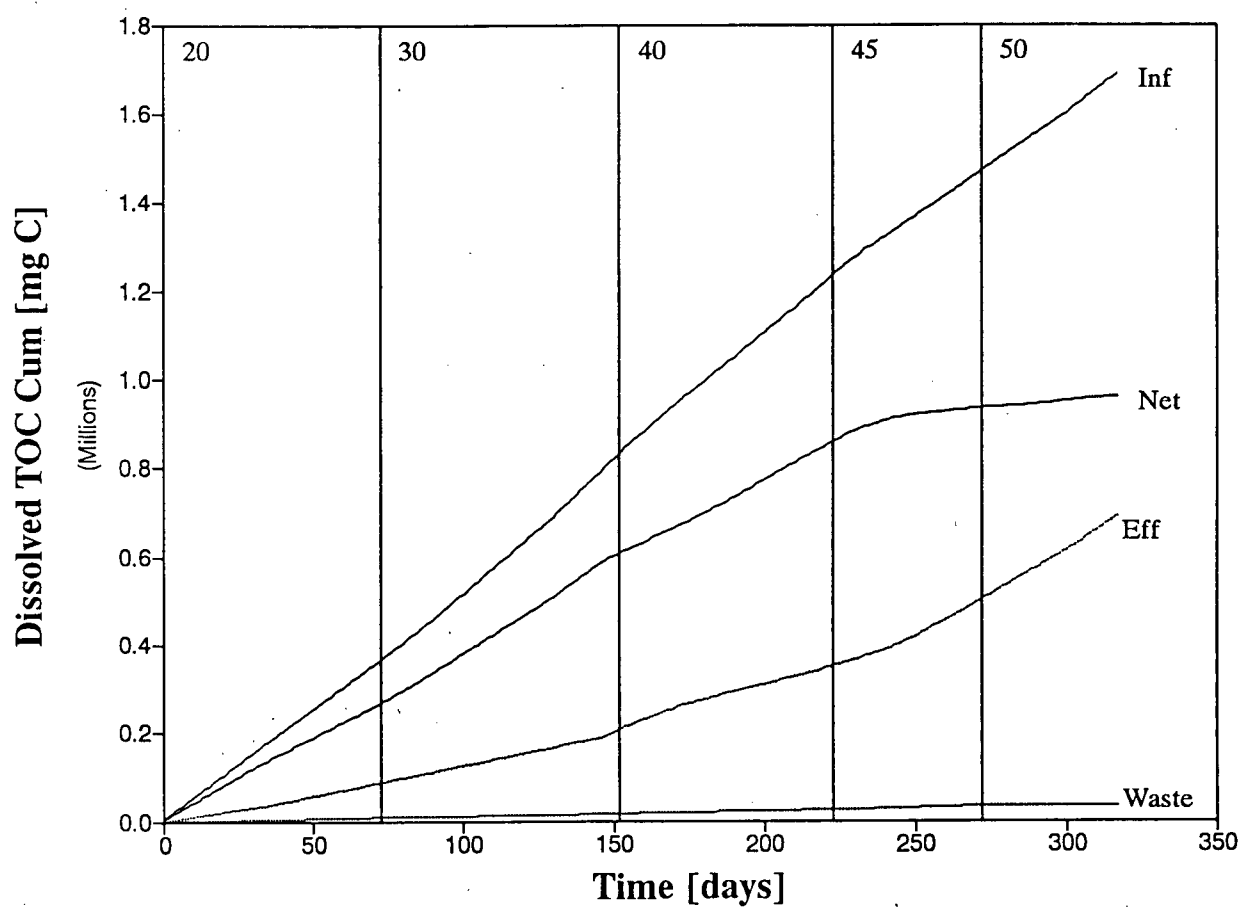


Figure A2. The cumulative TOC levels in the influent, effluent and wastage and the net TOC removal throughout the experimental period.

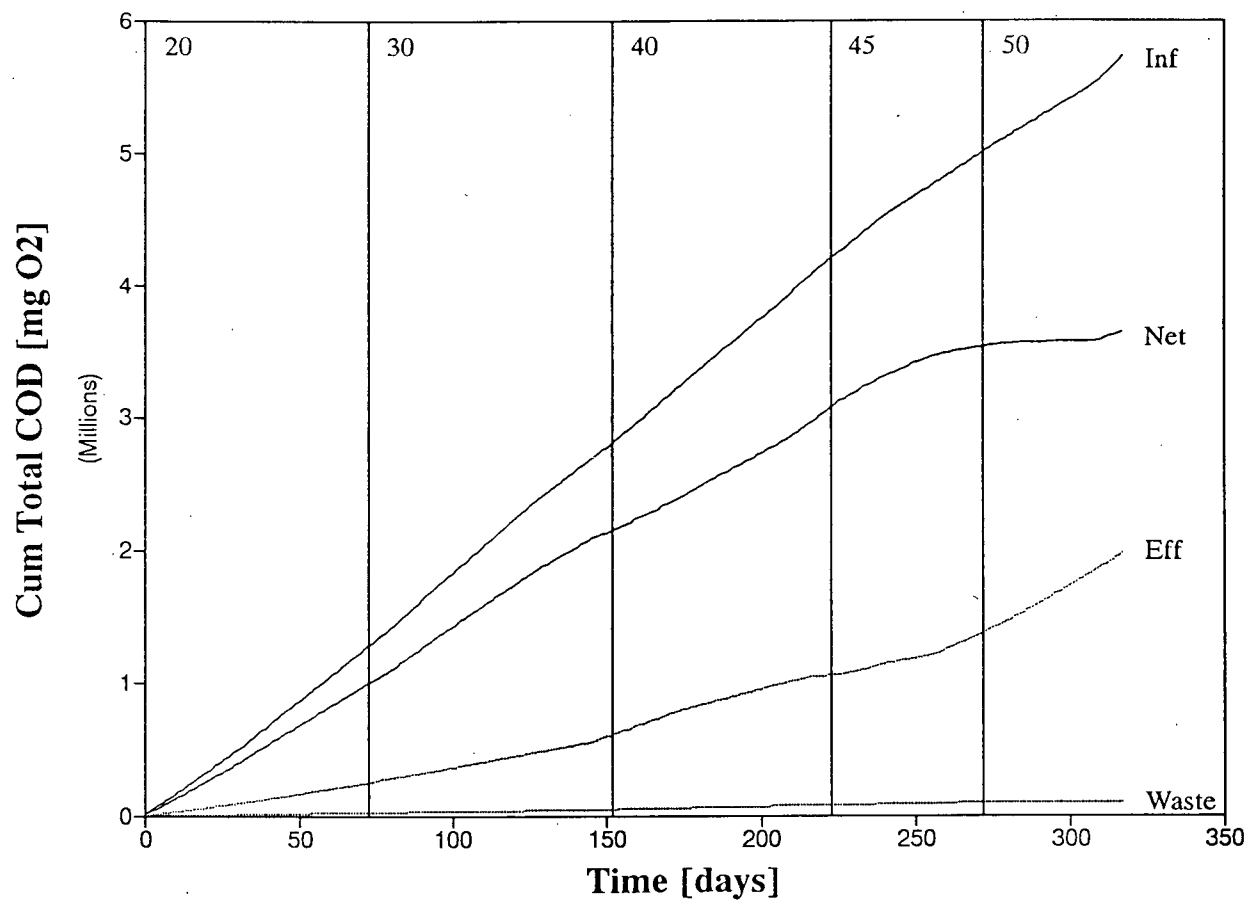


Figure A3. The cumulative TCOD in the influent, effluent and waste and the net TCOD removal throughout the experimental period.

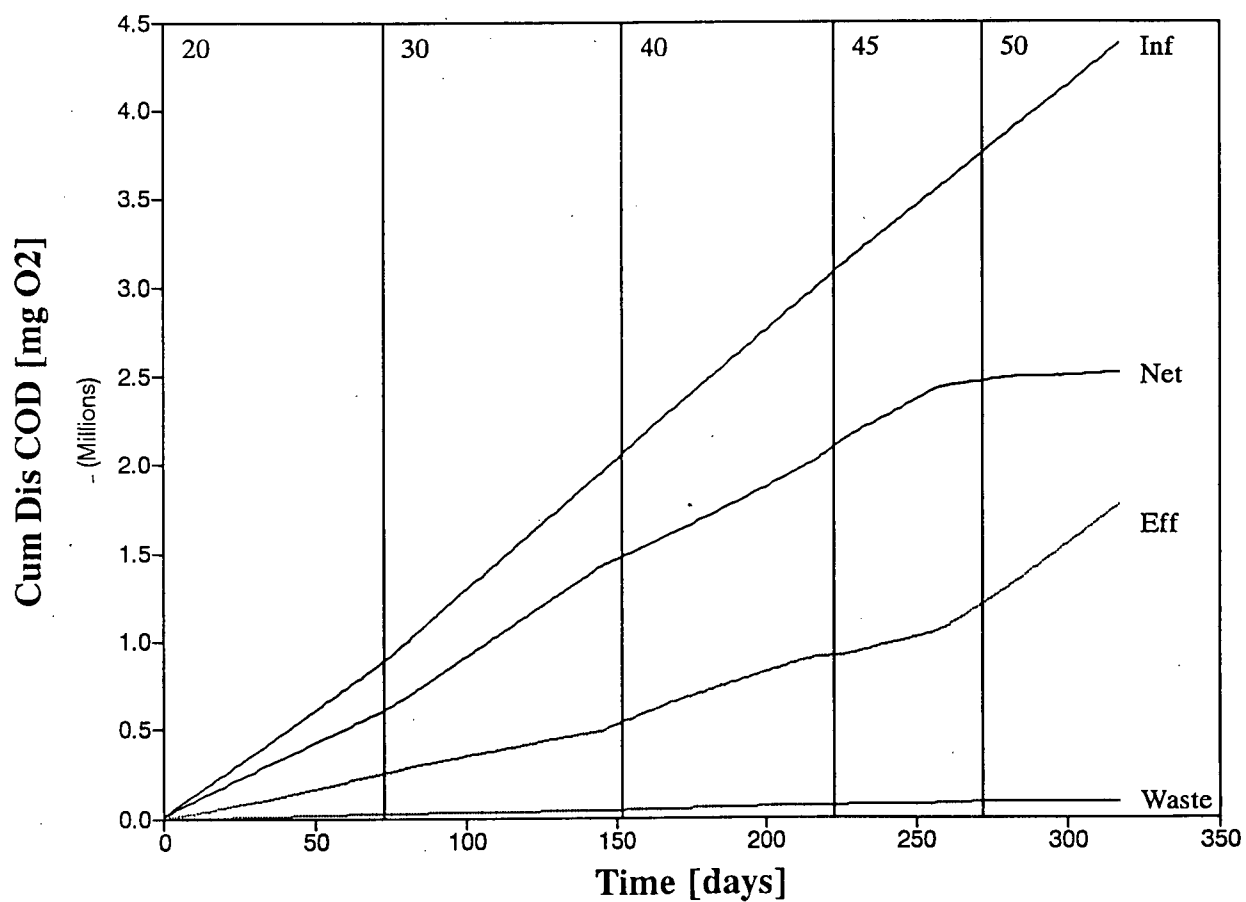


Figure A4. The cumulative DCOD in the influent, effluent and waste and the net DCOD removal throughout the experimental period.

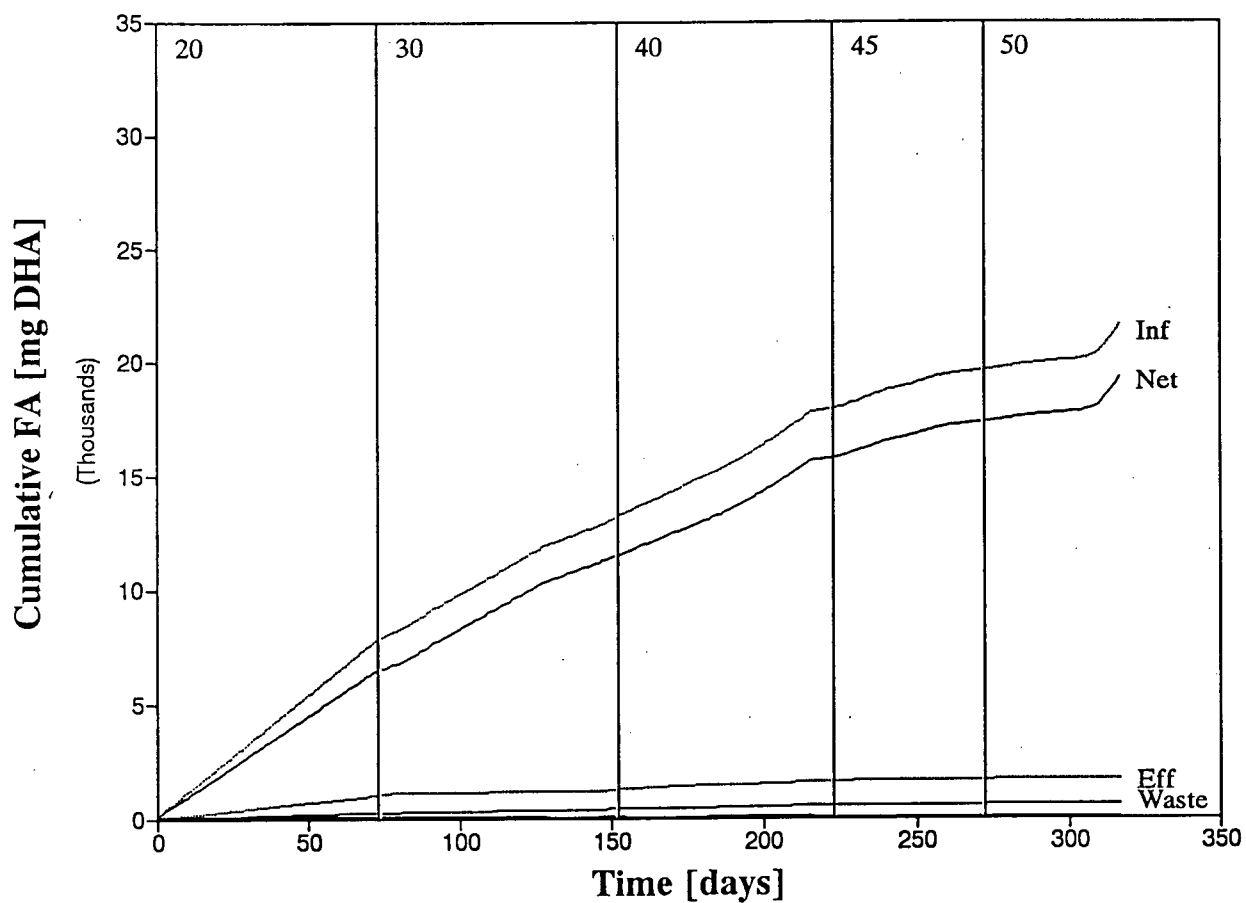


Figure A5. The cumulative totals of fatty acids for the influent, effluent, waste and net removal throughout the experimental period. The concentrations of fatty acids in the reactor were plotted on this graph but were negligible compared with the cumulative totals and are near the zero axis.



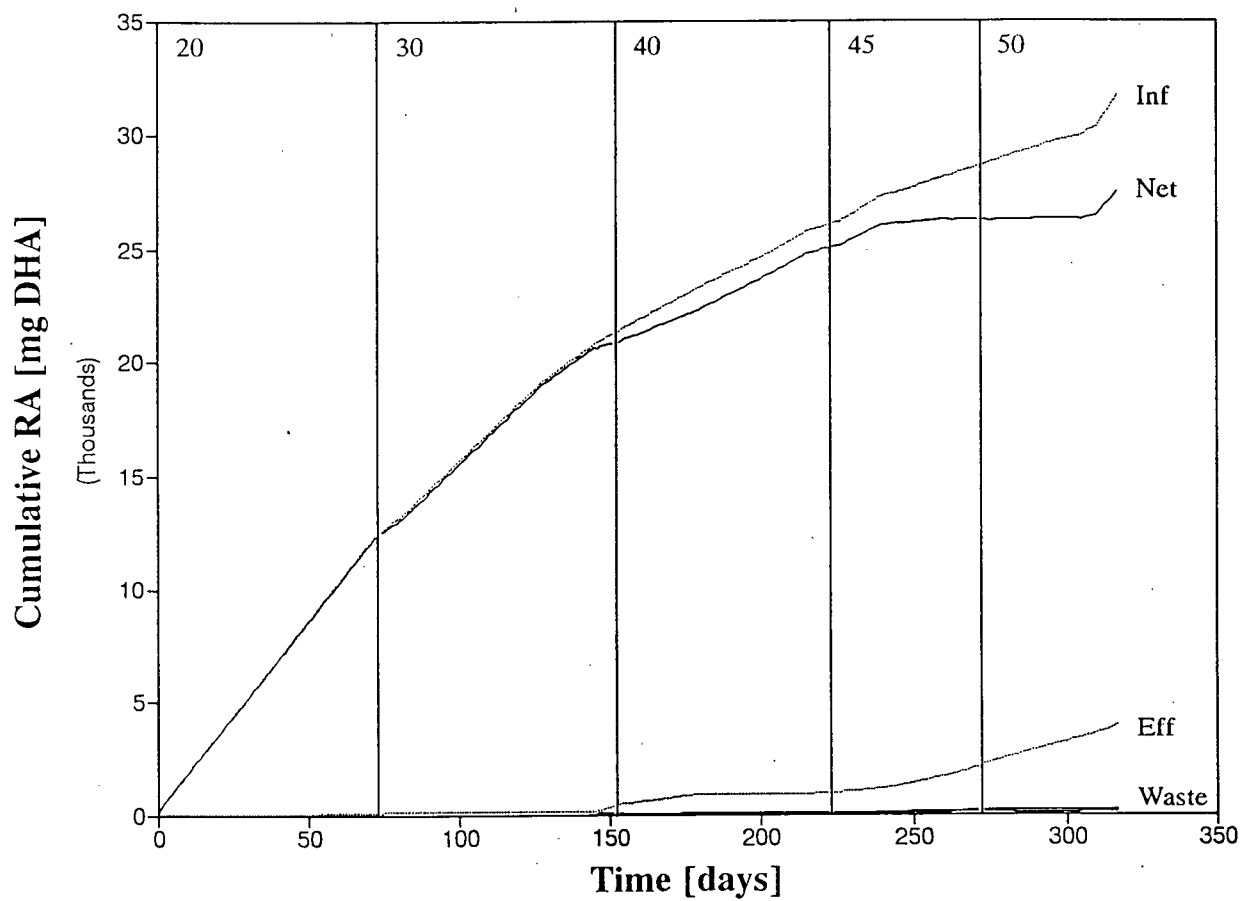


Figure A6. The cumulative totals of resin acids for the influent, effluent, waste and net removal throughout the experimental period. The concentrations of resin acids in the reactor were plotted on this graph but were negligible compared with the cumulative totals and are near the zero axis.

## **APPENDIX B: Details on the Calculation of RFA Removal Rates**

### **Observed Specific Removal Rates**

The observed specific removal rates examined the removal of fatty and resin acids in the solids and liquid phases during the complete react cycle, a 22.5 hour period. Thus,  $t$  in Equation 9 was 22.5 hours in the units of days and  $S_0$  was the resin or fatty acid concentration at time 0 of the react cycle and  $S$  was the resin or fatty acid concentration at 22.5 hours of the react cycle or at the end. Tables B1 and B2 detail the measurements used to calculate the observed specific removal rates.

Table B1. The fatty acid concentrations,  $S_o$  and  $S$ , the react cycle time ( $t$ ), the corresponding MLVSS concentration for the sampling days, and the calculated observed fatty acid specific removal rates.

Temp	Day	$S_o$	$S$	$t$	MLVSS	Observed Removal Rate
[°C]		[mg/L]	[mg/L]	[h]	[mg/L]	[mgRFA / mgMLVSS · d]
30	175	12.00	8.80	22.5	5110	0.000668
	214	5.10	3.74	22.5	5610	0.000259
40	266	9.63	0	22.5	4740	0.002167
	271	16.99	10.53	22.5	4730	0.001457
	278	12.16	9.74	22.5	4850	0.000532
	292	14.13	7.48	22.5	4590	0.001545
	301	12.12	8.71	22.5	4300	0.000846
45	320	10.04	3.88	22.5	5220	0.001259
	327	2.28	1.76	22.5	3910	0.000142
	334	8.35	3.13	22.5	3310	0.001682
	344	2.25	1.26	22.5	2600	0.000406
50	368	1.44	0.72	22.5	1830	0.00042
	383	1.31	0.62	22.5	2180	0.000338
	389	1.57	0.80	22.5	1750	0.000469
	395	5.00	2.00	22.5	1910	0.001675

Table B2. The resin acid concentrations,  $S_o$  and  $S$ , the react cycle time ( $t$ ), the corresponding MLVSS concentration for the sampling days, and the calculated observed resin acid specific removal rates.

Temp	Day	$S_o$	$S$	$t$	MLVSS	Observed Removal Rate
[°C]		[mg/L]	[mg/L]	[h]	[mg/L]	[mgRFA / mgMLVSS · d]
30	175	10.3	0	22.5	5110	0.00215
	214	4.87	0	22.5	5610	0.000926
40	266	6.52	0	22.5	4740	0.001467
	271	5.81	0.14	22.5	4730	0.001279
	278	4.65	0.14	22.5	4850	0.000992
	292	7.26	0	22.5	4590	0.001687
	301	5.36	0.13	22.5	4300	0.001297
45	320	12.56	10.46	22.5	5220	0.000429
	327	6.49	6.01	22.5	3910	0.000131
	334	13.26	12.10	22.5	3310	0.000374
	344	9.81	9.57	22.5	2600	0.000100
50	368	10.38	10.56	22.5	1830	-0.000100
	383	8.97	10.34	22.5	2180	-0.000670
	389	8.01	9.54	22.5	1750	-0.000930
	395	16.87	17.39	22.5	1910	-0.000290

### **Maximum Specific Removal Rates**

The maximum specific resin and fatty acid removal rates were calculated in a similar manner to the observed specific removal rates (Equation 9) except that the removal rates were calculated during the period of fastest removal starting near the beginning of the react cycle and not over the whole react cycle time as in the observed removal rates. A plot of the substrate concentration over the time of the react cycle helped in determining the period of fastest removal. Three or more data points had to be included in the time period of maximum removal, the first being between hour zero and hour two during the react cycle. The substrate concentrations ( $S_0$  and  $S$ ) are those seen at the beginning and at the end of this time period of maximum removal ( $t$ ) (Tables B3 and B4).

Table B3. The fatty acid concentrations,  $S_o$  and  $S$ , at the beginning and at the end of the time period ( $t$ ) of the maximum slope, the starting hour of this maximum slope ( $t_s$ ), the corresponding MLVSS concentration for the sampling days, and the calculated maximum fatty acid specific removal rates.

Temp	Day	$S_o$	$S$	$t$	$t_s$	MLVSS	Maximum Removal Rate
[°C]		[mg/L]	[mg/L]	[h]	[h]	[mg/L]	[mgRFA / mgMLVSS · d]
30	175	12.0	8.8	22.5	0	5110	0.000668
	214	5.1	3.74	22.5	0	5610	0.000259
40	266	9.63	6.0	6	0	4740	0.00306
	271	16.99	13.71	4	0	4730	0.00416
	278	12.16	9.74	22.5	0	4850	0.000532
	292	14.13	12.22	4	0	4590	0.00250
	301	12.55	8.71	21.5	1	4300	0.00100
45	320	9.99	7.68	3	1	5220	0.00354
	327	2.30	1.66	10	2	3910	0.000393
	334	8.36	6.9	3	1	3310	0.00353
	344	2.25	1.11	12	0	2600	0.000877
50	368	1.47	0.63	11	1	1830	0.00100
	383	1.31	0.94	2	0	2180	0.00204
	389	1.62	1.15	63	1	1750	0.00215
	395	5.85	3.28	10	2	1910	0.00323

Table B4. The resin acid concentrations,  $S_o$  and  $S$ , at the beginning and at the end of the time period ( $t$ ) of the maximum slope, the starting hour of this maximum slope ( $t_s$ ), the corresponding MLVSS concentration for the sampling days, and the calculated maximum resin acid specific removal rates.

Temp	Day	$S_o$	$S$	$t$	$t_s$	MLVSS	Maximum Removal Rate
[°C]		[mg/L]	[mg/L]	[h]	[h]	[mg/L]	[mgRFA / mgMLVSS · d]
30	175	10.3	6.4	2	0	5110	0.00916
	214	4.29	0.17	5	1	5610	0.00353
40	266	6.52	4.43	2	0	4740	0.00529
	271	5.18	0.7	10	2	4730	0.00227
	278	4.28	0.56	10	2	4850	0.00184
	292	7.07	3.53	10	2	4590	0.00185
	301	4.87	1.85	10	2	4300	0.00169
45	320	13.65	10.46	20.5	2	5220	0.000715
	327	6.72	5.95	10	1	3910	0.000473
	334	13.26	11.92	2	0	3310	0.00486
	344	9.81	9.57	22.5	0	2600	0.000100
50	368	10.49	9.96	17	1	1830	0.000409
	383	10.16	8.11	8	1	2180	0.00282
	389	9.89	9.54	21.5	1	1750	0.000223
	395	18.16	17.39	21.5	1	1910	0.000450

## **APPENDIX C: Individual RFA Removal Rates**

The maximum specific removal rates of individual resin and fatty acids have importance in determining which compounds degrade faster than others and through association with which phase, solid or liquid. This allows an understanding of the ease of RFA removal in whitewaters with different RFA compositions. For example, whitewaters containing large concentrations of certain RFAs with relatively higher removal rates might have their RFAs removed at a faster rate than other whitewaters of a different composition.

Table C1 lists the maximum specific removal rates for the individual fatty acids measured, palmitic, linoleic, oleic, and stearic acids. In the liquid phase of the fatty acid group, linoleic acid had the highest removal rate throughout the experimental period, followed by palmitic acid. Oleic and stearic had removal rates in the liquid phase of near zero and in many cases, none of these compounds were detected during the react cycle. In the solids phase, palmitic acid had the highest removal rates, followed by linoleic acid then oleic acid. Similar to the liquid phase, stearic acid had very low removal rates. No trends related to the different temperatures were discernible in any of the fatty acids in either the liquid or the solids phase.



Table C1. The maximum removal rates for the individual fatty acids, palmitic, linoleic, oleic, and stearic acids. n/a = no compound available for removal

Fatty Acid	Temp [°C]	Liquid		Solids	
		Average	SD	Average	SD
		[mg RFA / mg MLVSS·hr]		[mg RFA / mg MLVSS·hr]	
Palmitic	30	$-3.2 \times 10^{-7}$	0	$7.9 \times 10^{-6}$	0
	40	$6.2 \times 10^{-6}$	$3.5 \times 10^{-6}$	$4.8 \times 10^{-5}$	$2.3 \times 10^{-5}$
	45	$2.3 \times 10^{-5}$	$1.7 \times 10^{-5}$	$3.0 \times 10^{-5}$	$2.0 \times 10^{-5}$
	50	$1.4 \times 10^{-5}$	$1.1 \times 10^{-5}$	$1.5 \times 10^{-5}$	$6.2 \times 10^{-6}$
Linoleic	30	n/a	n/a	$2.4 \times 10^{-6}$	0
	40	$1.8 \times 10^{-5}$	$2.8 \times 10^{-6}$	$1.9 \times 10^{-5}$	$1.2 \times 10^{-5}$
	45	$2.1 \times 10^{-5}$	0	$8.8 \times 10^{-6}$	$1.1 \times 10^{-5}$
	50	$2.0 \times 10^{-5}$	$5.9 \times 10^{-6}$	$3.1 \times 10^{-5}$	$1.7 \times 10^{-5}$
Oleic	30	n/a	n/a	$1.1 \times 10^{-5}$	0
	40	n/a	n/a	$1.2 \times 10^{-5}$	$9.0 \times 10^{-6}$
	45	n/a	n/a	$3.2 \times 10^{-6}$	$3.5 \times 10^{-6}$
	50	$3.7 \times 10^{-6}$	$6.2 \times 10^{-7}$	$9.8 \times 10^{-6}$	$5.8 \times 10^{-6}$
Stearic	30	n/a	n/a	$7.9 \times 10^{-7}$	0
	40	$1.0 \times 10^{-5}$	$6.7 \times 10^{-6}$	$3.3 \times 10^{-6}$	$3.9 \times 10^{-6}$
	45	n/a	n/a	$2.9 \times 10^{-6}$	$2.9 \times 10^{-6}$
	50	n/a	n/a	$2.5 \times 10^{-6}$	$3.2 \times 10^{-6}$

Table C2 lists the maximum removal rates of the individual resin acids measured, pimaric, sandaracopimaric, isopimaric, palustric and levopimaric, dehydroabietic, abietic, and neoabietic acids. In the liquid phase, DHA had the highest removal rates, followed closely by abietic then palustric and levopimaric acids. Isopimaric and when present, neoabietic, had intermediate removal rates and sandaracopimaric and pimaric acids had removal rates near zero. No trends were observed in relation to temperature except in the sandaracopimaric acid content of the liquid phase which decreased with temperature.

Table C2. The maximum removal rates of the individual resin acids measured, pimaric, sandaracopimaric, isopimaric, palustric and levopimaric, dehydroabietic, abietic, and neoabietic acids. n/a = no compound available for removal

Resin Acid	Temp [°C]	Liquid		Solids	
		Average	SD	Average	SD
		[mg RFA / mg MLVSS·hr]		[mg RFA / mg MLVSS·hr]	
Pimaric	30	1.5 x 10 <sup>-5</sup>	0	1.2 x 10 <sup>-5</sup>	0
	40	1.5 x 10 <sup>-6</sup>	1.5 x 10 <sup>-6</sup>	1.4 x 10 <sup>-6</sup>	1.2 x 10 <sup>-6</sup>
	45	3.4 x 10 <sup>-6</sup>	2.8 x 10 <sup>-6</sup>	2.4 x 10 <sup>-6</sup>	2.5 x 10 <sup>-6</sup>
	50	5.5 x 10 <sup>-6</sup>	5.3 x 10 <sup>-6</sup>	2.2 x 10 <sup>-5</sup>	4.0 x 10 <sup>-5</sup>
Sandaracopimaric	30	n/a	n/a	n/a	n/a
	40	6.9 x 10 <sup>-6</sup>	6.4 x 10 <sup>-6</sup>	-1.1 x 10 <sup>-5</sup>	1.3 x 10 <sup>-5</sup>
	45	2.1 x 10 <sup>-6</sup>	1.3 x 10 <sup>-6</sup>	- 1.4 x 10 <sup>-6</sup>	3.8 x 10 <sup>-6</sup>
	50	1.5 x 10 <sup>-6</sup>	2.1 x 10 <sup>-6</sup>	-1.3 x 10 <sup>-6</sup>	2.5 x 10 <sup>-6</sup>
Isopimaric	30	n/a	n/a	n/a	n/a
	40	9.6 x 10 <sup>-6</sup>	3.1 x 10 <sup>-6</sup>	5.9 x 10 <sup>-6</sup>	4.2 x 10 <sup>-6</sup>
	45	1.6 x 10 <sup>-5</sup>	1.7 x 10 <sup>-5</sup>	1.6 x 10 <sup>-6</sup>	2.3 x 10 <sup>-6</sup>
	50	7.3 x 10 <sup>-6</sup>	1.8 x 10 <sup>-5</sup>	4.6 x 10 <sup>-6</sup>	1.3 x 10 <sup>-5</sup>
Palustric & Levopimaric	30	n/a	n/a	n/a	n/a
	40	1.4 x 10 <sup>-5</sup>	1.3 x 10 <sup>-5</sup>	3.0 x 10 <sup>-5</sup>	5.7 x 10 <sup>-5</sup>
	45	8 x 10 <sup>-6</sup>	5.8 x 10 <sup>-6</sup>	1.5 x 10 <sup>-5</sup>	1.7 x 10 <sup>-5</sup>
	50	1.1 x 10 <sup>-5</sup>	7.0 x 10 <sup>-6</sup>	2.4 x 10 <sup>-5</sup>	2.3 x 10 <sup>-5</sup>

Dehydroabietic	30	$5.9 \times 10^{-5}$	0	$1.6 \times 10^{-5}$	0
	40	$1.9 \times 10^{-5}$	$1.1 \times 10^{-5}$	$5.7 \times 10^{-6}$	$1.1 \times 10^{-6}$
	45	$1.4 \times 10^{-4}$	$2.6 \times 10^{-4}$	$4.0 \times 10^{-6}$	$3.7 \times 10^{-6}$
	50	$1.4 \times 10^{-5}$	$2.8 \times 10^{-5}$	$2.5 \times 10^{-5}$	$2.8 \times 10^{-5}$
Abietic	30	$3.3 \times 10^{-5}$	0	$1.2 \times 10^{-5}$	0
	40	$8.2 \times 10^{-6}$	$6.3 \times 10^{-6}$	$6.7 \times 10^{-6}$	$4.9 \times 10^{-6}$
	45	$4.7 \times 10^{-6}$	$6.0 \times 10^{-6}$	$3.3 \times 10^{-6}$	$3.7 \times 10^{-6}$
	50	$1.4 \times 10^{-5}$	$1.2 \times 10^{-5}$	$7.3 \times 10^{-6}$	$5.8 \times 10^{-6}$
Neoabietic	30	$6.7 \times 10^{-6}$	0	n/a	n/a
	40	$9.6 \times 10^{-6}$	$4.7 \times 10^{-6}$	n/a	n/a
	45	$-1.2 \times 10^{-7}$	$2.6 \times 10^{-6}$	$4.9 \times 10^{-6}$	$7.4 \times 10^{-7}$
	50	$6.5 \times 10^{-5}$	$1.1 \times 10^{-5}$	$5.8 \times 10^{-7}$	$1.0 \times 10^{-6}$

## APPENDIX D: Raw Experimental Data

Table D1 details the volumes wasted from the reactor during certain time periods.

Table D1. The volumes wasted from the reactor during certain time periods.

Volume Wasted [L]	Time Period [days]
0.5	0 to 65
0.3	66 to 164
0	165 to 169
0.3	170 to 276
0.1	277 to 280
0	282 to 318

Pages 174 and 175 contain the raw experimental data for the influent and effluent of TCOD, DCOD, TOC, TDS and VSS and the MLVSS.

Pages 176 through 234 detail the resin and fatty acid raw experimental data. For these data, time is in hours and the resin and fatty acid concentration is in mg/L. Time -1.5 is the sample point at the end of the previous cycle, at 22.5 hours. Effnext is the effluent at the end of the measured cycle, while Eff is the effluent right before the measured cycle.

Time [day]	Temp [oC]	TCOD Inf [mg/LO2]	TCOD Eff [mg/LO2]	DCOD Inf [mg/LO2]	DCOD Eff [mg/LO2]	TOC Inf [mg/L C]
0	20	2818		2385		1000
6	20	2818	689	2385	559	1040
18	20					
33	20	3858	611	2298	793	953
73	30	3486	1092	2598	905	1012
77	30					
81	30	3733		2992	776	1068
90	30	4621	855	3190	737	1115
117	30					
129	30	3397	917	2721	630	1202
146	34					
148	37					
150	39					
152	40					
154	40	3734	1812	3126	1575	1363
160	40					
173	40	4086	1574	2814	1172	1016
181	40	4286	1306	2948	1172	1133
186	40	3617	1306	2747	1155	1031
193	40	3818	1339	2948	1239	1155
207	40	3929	1257	2750	1022	1085
216	40	4558	1218	2829	1002	1124
217	43					
220	44					
223	45					
226	45	3262	349	2951	302	1224
235	45	4383	1831	2640	1271	843
242	45	2722	680	2722	680	933
249	45	3234	969	2786	905	978
256	45	2593	1129	2722	937	890
259	45	3259	2268	2730	2003	975
263	47					
266	49					
272	50					
276	50	2796	2202	2796	2334	944
283	50	2862	2532	2730	2400	882
298	50	2730	2796	2532	2664	936
304	50	2824	2824	2950	2572	1083
310	50	3642	2824	2950	2698	1050
317	50	5530	2950	2824	2635	1016

Time [day]	TOC Eff [mg/L C]	MLVSS [mg/L]	VSS Eff [mg/L]	VSS Inf [mg/L]	TDS Inf [mg/L]	TDS Eff [mg/L]
0		5850		172	3820	
6	221	5060	80	208	4276	4104
18		5190	132	320	3224	2096
33	235	3770	276	628	3004	1988
73	359	5670	204	288	3476	2120
77		5910	508			
81	279	5260	652	204	3160	1948
90	290	5110	124	420	3244	2104
117		6050	416	624	3052	2104
129	298	5610	224	376	2984	2048
146		4820				
148		4890				
150		4710				
152		4650				
154	662	5360	628	156	3744	3324
160		4930	520	510		
173	419	5350	144	672	4328	2576
181	376	4740	148	492	4060	2700
186	405	4730	92	416	3968	2524
193	322	4850	100	340	3284	2500
207	379	4590	140	408	3396	2456
216	336	4300	68	584	3424	2240
217		3650				
220		5780	148			
223		5110				
226	462	4890	296	152	3852	2492
235	403	5220	360	764		2400
242	557	3910	0	68	3180	3024
249	786	3310	204	224	4356	3988
256	816	2760	216	76	3912	4064
259	762	2600	156	140	4104	3796
263		2290	124			
266		2300	72			
272		1850	72			
276	854	1950	92	68	4752	4680
283	825	1830	120	80	3376	3608
298	729	2180	156	60	4652	4388
304	936	1750	176	92	5160	4868
310	962	1910	96	452	5068	5032
317	894	1600	212	1928	4836	4732

December 15, 1993

Time	Palmitic	Linoleic	Oleic	Stearic	FA
Inf1	13.3	4.5	3.2	2.1	23.1
Inf2	12.8	4.2	2.9	0.96	20.9
Inf3	12.2	4.2	2.9	0.94	20.2
Eff1	1.8	0	0	0	1.8
Eff2	3.3	0.3	0	0.38	4
Eff3	3.4	0	0	0.25	3.6

Time	Pimaric	Sandara	Isopimaric	Palus+Lev	DHA
Inf1	3	0.96	7.9	5.1	12.1
Inf2	3	0.98	7.7	4.2	12.6
Inf3	2.9	0.96	7.5	3.3	12.4
Eff1	0	0	0	0	0
Eff2	0	0	0	0	0.41
Eff3	0	0	0	0	0.32

Time	Abietic	Neoabietic	RA	RFA
Inf1	6.3	0	35.3	58.5
Inf2	5.7	0.84	34.9	55.8
Inf3	4.3	0.21	31.8	52
Eff1	0	0	0	1.8
Eff2	0	0	0.41	4.4
Eff3	0	0	0.32	4

January 25, 1994

Time	Palmitic	Linoleic	Oleic	Stearic	FA
Inf1	3.6	3.9	0	0.29	7.8
Inf2	5.4	6.3	2.8	0.39	14.8
0	7.4	0.88	0.48	0.38	9.1
0.5	8.9	1.1	0.4	0.47	10.8
1	10	1	0.31	0.53	11.9
2	10	1	0.33	0.54	12.1
3	10.2	1	0.31	0.53	12
4	10.6	1	0.35	0.55	12.6
5	11.9	1	0.3	0.64	13.9
6	10.8	0.86	0.33	0.59	12.6
EffAvg	2.35	1.15	0.55	0.12	4.2
Eff1	3.2	2.3	1.1	0.24	6.9
Eff2	1.5	0	0	0	1.5



January 25, 1994

Time	Pimaric	Sandara	Isopimaric	Palus+Lev	DHA
Inf1	1.2	0.4	3.4	1.7	5.6
Inf2	1.8	0.6	5.1	2.9	9.1
0	0.62	0.2	1.7	1.1	3
0.5	0.55	0	1.1	0.87	2.9
1	0.39	0	0.7	0.77	2.9
2	0	0	0	0.59	2.7
3	0	0	0	0	1.2
4	0	0	0	0	0.22
5	0	0	0	0	0.35
6	0	0	0	0	0.32
EffAvg	0.3	0.095	0.8	0.23	1.75
Eff1	0.6	0.19	1.6	0.46	3.5
Eff2	0	0	0	0	0

January 25, 1994

Time	Abietic	Neoabietic	IRA	RFA
Inf1	2.2	0.26	14.8	22.6
Inf2	3.6	0.44	23.6	38.4
0	1.6	0.24	8.4	17.5
0.5	1.3	0	6.8	17.6
1	1.2	0	6	17.9
2	0.72	0	4	16.1
3	0	0	1.2	13.2
4	0	0	0.22	12.8
5	0	0	0.35	14.2
6	0	0	0.32	12.9
EffAvg	0.33	0	3.45	7.65
Eff1	0.66	0	6.9	13.8
Eff2	0	0	0	1.5

February 1, 1994

Time		Palmitic	Linoleic	Oleic	Stearic	FA
Inf1		5	5.6	2.1	0.6	12.3
Inf2		4.3	4.3	2	0.5	11.1
Inf3		4.9	4.5	2.1	0.6	12.1
	0	8	0.75	0.39	0.53	9.6
1/2		8.9	0.84	0.42	0.57	10.7
	1	9	0.79	0.39	0.57	10.8
	2	10.7	0.82	0.44	0.69	12.7
	3	10.4	0.99	0.37	0.67	12.4
	4	11	0.9	0.39	0.72	13
	5	9.2	0.74	0.35	0.6	10.9
	6	9.6	0.81	0.32	0.64	11.4
EffAvg	23.75	0.8	0	0	0	0.8
Eff1		0.81				0.81
Eff2		0.82				0.82
Eff3		0.77				0.77

February 1, 1994

Time		Pimaric	Sandara	Isopimaric	Palus+LevDHA	
Inf1		1.5	1.2	3.7	2.5	7
Inf2		1.5	1.2	3.6	1.6	7.7
Inf3		1.5	1.2	3.9	2.9	7
	0	1.1	0.36	1		2.8
1/2		0.95		0.73		2.7
	1	0.81			0.19	2.7
	2	0.62				2.6
	3	0.48				1.3
	4	0.43				0.28
	5	0.32				0.24
	6	0.32				0.22
EffAvg	23.75	0	0	0	0	0
Eff1						
Eff2						
Eff3						

February 1, 1994

Time		Abietic	Neoabietic	RA	RFA
Inf1		3.4	0.25	19.61	31.87
Inf2		2.2	0.26	18.14	29.21
Inf3		3.7	0.2	20.5	32.6
	0	0.74	0.14	6.2	15.9
1/2		0.75	0.13	5.2	16
	1	0.53	0.12	4.3	15.1
	2	0.23	0.11	3.6	16.2
	3	0.08	0.07	1.9	14.3
	4	0		0.71	13.7
	5	0		0.56	11.5
	6	0		0.54	11.9
EffAvg	23.75	0	0	0	0.8
Eff1					0.81
Eff2					0.82
Eff3					0.77

February 10, 1994

Time		Palmitic	Linoleic	Oleic	Stearic	FA
Inf1		8	8.3	3.9	0.53	20.7
Inf2		7.4	8.5	3.9	0.5	20.3
Inf3		7.7	8	3.7	0.52	19.9
	-1.5	6.9	0.5	0.34	0	7.8
	0	9.7	0.91	0.74	0.65	12
	1	9.3	0.98	0.47	0.57	11.3
	2	9.5	0.96	0.56	0.59	11.6
	4	8.3	0.97	0.37	0.51	10.2
	6	9.5	1.1	0.47	0.51	11.5
	9	10.2	1.1	0.48	0.53	12.2
	12	10.2	0.98	0.45	0.54	12.1
	23	7.5	0.62	0.34	0.36	8.8
EffAvg	23.75	0.114333	0	0	0	0.114333
Eff1		0.085				0.085
Eff2		0.068				0.068
Eff3		0.19				0.19

February 10, 1994

Time	Pimaric	Sandara	Isopimaric	Palus+Lev	DHA
Inf1	2.8	1.1	7.5	1.9	12.4
Inf2	2.9	2.4	7.7	2.5	11.6
Inf3	2.8	2	7.3	2.2	11.7
-1.5	0	0	0	0	0
0	1.2	0.47	2.5	0	5.2
1	0.94	0	1.5	0	5.6
2	0.62	0.22	0.7	0	4.4
4					3.7
6					0.36
9					0.26
12					0
23					0
EffAvg	23.75	0	0	0	0
Eff1					
Eff2					
Eff3					

February 10, 1994

Time	Abietic	Neoabietic	RA	RFA
Inf1	3.5	0	29.3	49.9
Inf2	4.8	0.32	32.2	52.5
Inf3	4.2	0.28	30.5	50.4
-1.5	0	0	0	7.8
0	0.91	0	10.3	22.3
1	0.93	0	8	19.3
2	0.41	0	6.4	18
4	0	0	3.7	13.9
6	0	0	0.36	11.9
9	0	0	0.26	12.5
12	0	0	0	12.1
23	0	0	0	8.8
EffAvg	23.75	0	0	0.114333
Eff1				0.085
Eff2				0.068
Eff3				0.19

March 21, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	3.4	4.2	1.6	0.42	9.6
	Inf2	3.4	4.4	1.6	0.41	9.9
	Inf3	3.4	4.3	1.6	0.38	9.7
Liquid	-1.5	0	0	0	0	0
	0	0.1	0	0	0	0.1
	1	0.12	0	0	0	0.12
	2	0	0	0	0	0
	4	0.11	0	0	0	0.11
	6	0	0	0	0	0
	9	0	0	0	0	0
	12	0	0	0	0	0
	23	0.14	0	0	0	0.14
Solid	-1.5	3.6	0.18	0	0.23	4
	0	4.3	0.28	0.12	0.26	5
	1	4.1	0.28	0.12	0.26	4.8
	2	3.9	0.26	0	0.23	4.4
	4	4.1	0.23	0	0.27	4.7
	6	3.7	0.2	0	0.23	4.1
	9	3.6	0.21	0	0.22	4
	12	3.8	0.22	0	0.24	4.2
	23	3.3	0.17	0	0.21	3.6
EffAvg	23.75	0.076667	0	0	0	0.076667
	Eff1	0.1				0.1
	Eff2	0.13				0.13
	Eff3	0				0

March 21, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	1.4	0.42	3.8	3.4	5.3
	Inf2	1.5	0.44	3.9	3.6	5.5
	Inf3	1.4	0.41	3.7	3.7	5.2
Liquid	-1.5	0	0	0	0	0
	0	0.33	0	0	0.84	2
	1	0.24	0	0	0.71	1.8
	2	0.17	0	0	0.67	1.7
	4	0	0	0	0.37	1.5
	6	0	0	0	0	0
	9	0	0	0	0	0
	12	0	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	0	0	0	0	0
	0	0.13	0	0	0	0.36
	1	0.13	0	0	0.2	0.37
	2	0	0	0	0	0.43
	4	0	0	0	0	0
	6	0	0	0	0	0.17
	9	0	0	0	0	0
	12	0	0	0	0	0
	23	0	0	0	0	0
EffAvg	23.75	0	0	0	0	0
	Eff1					
	Eff2					
	Eff3					

March 21, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	3.5	0.9	18.8	28.4
	Inf2	3.7	0.94	19.6	29.4
	Inf3	3.8	1.2	19.5	29.2
Liquid	-1.5	0	0	0	0
	0	0.74	0.15	4.1	4.2
	1	0.56	0	3.3	3.4
	2	0.49	0.13	3.1	3.1
	4	0	0	1.9	2
	6	0	0	0	0
	9	0	0	0	0
	12	0	0	0	0
	23	0	0	0	0.14
Solid	-1.5	0	0	0	4
	0	0.27	0	0.77	5.7
	1	0.29	0	0.99	5.8
	2	0.2	0	0.64	5
	4	0	0	0	4.7
	6	0	0	0.17	4.3
	9	0	0	0	4
	12	0	0	0	4.2
	23	0	0	0	3.6
EffAvg	23.75	0	0	0	0.076667
	Eff1				0.1
	Eff2				0.13
	Eff3				0

April 15, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.88	0.27	2.79	1.59	4.89
	Inf2	0.85	0.4	4.92	1.61	5.03
	Inf3	0.94	0.29	2.9	1.75	5.15
Liquid	-1.5	0.74	0	1.49	0.69	3.62
	0	0.88	0.22	2.02	1.8	4.26
	1	0.9	0.24	2.07	1.82	4.44
	2	0.94	0.24	2.07	1.72	4.37
	4	0.95	0.23	2.01	1.73	4.59
	6	0.78	0.19	1.65	1.34	3.74
	9	0.98	0.23	2.04	1.52	4.75
	12	1	0.23	2	1.46	4.79
	23	0.96	0.2	1.95	1.13	4.73
Solid	-1.5	0.54	0	1.24	0	0.81
	0	0.48	0	1.28	0.4	0.96
	1	0.45	0	1.29	0.47	0.87
	2	0.46	0	1.27	0.37	0.85
	4	0.49	0	1.26	0.47	0.82
	6	0.55	0	1.33	0.23	0.9
	9	0.58	0	1.44	0.26	0.91
	12	0.58	0	1.47	0	0.9
	23	0.54	0	1.4	0.36	0.85
NowEffAv	23.75	0.756667	0.093333	1.466667	0.366667	3.213333
Now	Eff1	0.84	0.15	1.62	0.6	3.57
	Eff2	0.71	0	1.36	0	3.03
	Eff3	0.72	0.13	1.42	0.5	3.04
NextEffAv		0.983333	0.186667	1.973333	1.13	4.62
Next	Eff1	0.89	0.18	1.97	1.09	4.6
	Eff2	1.01	0.19	1.92	1.14	4.53
	Eff3	1.05	0.19	2.03	1.16	4.73



April 15, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	7	3.66	1.12	0.44	12.3
	Inf2	7.21	3.76	1.18	0.58	12.7
	Inf3	7.11	3.91	1.22	0.57	12.8
Liquid	-1.5	0.75	0	0	0	0.75
	0	0.8	0.46	0	0	1.26
	1	1.58	0.4	0	0.14	2.12
	2	0.75	0.21	0	0	0.95
	4	1.29	0	0	0.16	1.46
	6	0.83	0.13	0	0	0.96
	9	1.1	0	0	0	1.1
	12	1.17	0	0	0.15	1.32
	23	0.45	0	0	0	0.45
Solid	-1.5	5.31	0.44	0.13	0.61	6.49
	0	10.5	1	0.63	0.93	14.1
	1	8.67	1.5	0.53	0.89	11.6
	2	6.5	1.15	0.44	0.72	8.82
	4	8.1	0.59	0.18	0.77	9.64
	6	7.7	0.63	0.2	0.8	9.33
	9	7.32	0.51	0.15	0.72	8.69
	12	5.96	0.46	0.14	0.61	7.17
	23	4.08	0.56	0.15	0.49	5.28
NowEffAv	23.75	2.196667	0.25	0	0.306667	2.756667
Now	Eff1	2.52	0.19	0	0.31	3.03
	Eff2	2.08	0.29	0	0.32	2.69
	Eff3	1.99	0.27	0	0.29	2.55
NextEffAv		2.62	0.203333	0	0.306667	3.136667
Next	Eff1	2.53	0.19	0	0.32	3.05
	Eff2	2.61	0.24	0	0.32	3.17
	Eff3	2.72	0.18	0	0.28	3.19

April 15, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	2.09	0.6	13.1	25.4
	Inf2	2.1	0.6	15.5	28.2
	Inf3	2.19	0.64	13.9	26.7
Liquid	-1.5	1.57	0	8.12	8.87
	0	2.12	0.52	11.8	13.1
	1	2.19	0.54	12.2	14.3
	2	2.16	0.51	12	13
	4	2.17	0.52	12.2	13.7
	6	1.76	0.43	9.89	10.9
	9	2.14	0.49	12.2	13.3
	12	2.16	0.45	12.1	13.4
	23	1.96	0	10.9	11.4
Solid	-1.5	0.87	0	3.46	9.95
	0	0.91	0.18	4.22	18.3
	1	0.83	0.18	4.09	15.7
	2	0.84	0.2	4	12.8
	4	0.89	0.19	4.12	13.8
	6	1	0	3.98	13.3
	9	1	0	4.19	12.9
	12	0.98	0	3.93	11.1
	23	0.88	0	4.04	9.32
NowEffAv	23.75	1.456667	0	7.35	10.11333
Now	Eff1	1.59	0	8.37	11.4
	Eff2	1.39	0	6.48	9.18
	Eff3	1.39	0	7.2	9.76
NextEffAv		1.936667	0	10.8	13.96667
Next	Eff1	1.89	0		

May 12, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	4.7	5.28	1.37	0.3	11.6
	Inf2	4.64	5.43	1.69	0.3	12.1
	Inf3	4.43	5.28	1.65	0.29	11.7
Liquid	-1.5	0.09	0	0	0	0.09
	0	0.58	0	0	0	0.58
	1	0.58	0	0	0	0.58
	2	0.47	0	0	0	0.47
	4	0.41	0	0	0	0.41
	6	0.42	0	0	0	0.42
	9	0.34	0	0	0	0.34
	12	0.22	0	0	0	0.22
Solid	-1.5	3.48	0.15	0	0.25	3.88
	0	7.02	0.84	0.61	0.58	9.05
	1	7.25	0.53	0.42	0.59	8.79
	2	6.55	0.42	0.31	0.52	7.8
	4	5.59	0.27	0.12	0.47	6.45
	6	4.88	0.23	0.09	0.39	5.58
	9	5.02	0.24	0.1	0.45	5.82
	12	4.61	0.2	0.1	0.34	5.25
EffAv	23.75	0.133333	0	0	0	0.133333
	Eff1	0.17	0	0	0	0.17
	Eff2	0	0	0	0	0
	Eff3	0.23	0	0	0	0.23
	EffS	0.12	0	0	0	0.12

May 12, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.99	0.43	3.11	1.97	4.64
	Inf2	0.96	0.41	2.99	1.98	4.21
	Inf3	0.93	0.4	2.9	1.95	4.35
Liquid	-1.5	0	0	0	0	0
	0	0.29	0.12	0.75	0.81	1.78
	1	0.3	0.12	0.72	0.52	1.74
	2	0.28	0	0.63	0	1.59
	4	0.27	0	0.54	0	1.18
	6	0.28	0	0.5	0.26	0.98
	9	0.29	0	0.41	0	0.37
	12	0.19	0	0	0	0
Solid	-1.5	0	0	0	0	0
	0	0.23	0	0.75	0.16	0.36
	1	0.23	0	0.68	0	0.37
	2	0.22	0	0.6	0	0.32
	4	0.24	0	0.58	0	0.27
	6	0.25	0	0.51	0	0.19
	9	0.25	0	0.47	0	0.11
	12	0.15	0	0	0	0
EffAv	23.75	0	0	0	0	0
	Eff1	0	0	0	0	0
	Eff2	0	0	0	0	0
	Eff3	0	0	0	0	0
	EffS	0	0	0	0	0

May 12, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	2.76	0.77	14.7	26.3
	Inf2	2.72	0.83	14.1	26.2
	Inf3	2.48	0.7	13.7	25.4
Liquid	-1.5	0	0	0	0.09
	0	0.77	0.15	4.67	5.25
	1	0.7	0.14	4.23	4.82
	2	0.55	0	3.05	3.52
	4	0.42	0.23	2.64	3.05
	6	0.15	0	2.18	2.6
	9	0	0	1.06	1.41
	12	0	0	0.19	0.41
Solid	-1.5	0	0	0	3.88
	0	0.35	0	1.85	10.9
	1	0.31	0	1.58	10.4
	2	0.24	0	1.38	9.18
	4	0.17	0	1.26	7.71
	6	0	0	0.94	6.52
	9	0	0	0.83	6.64
	12	0	0	0.15	5.4
EffAv	23.75	0	0	0	0.133333
	Eff1	0	0	0	0.17
	Eff2	0	0	0	0
	Eff3	0	0	0	0.23
	EffS	0	0	0	0.12

May 17, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	6.1	5.33	1.26	0.4	13.1
	Inf2	6.53	5.38	1.3	0.45	13.6
	Inf3	6.45	5.38	1.29	0.43	13.5
Liquid	-1.5	0.14	0	0	0	0.14
	0	0.75	0.15	0	0.08	0.99
	1	0.45	0.08	0	0	0.52
	2	0.39	0	0	0	0.39
	4	0.31	0	0	0	0.31
	6	0.26	0	0	0	0.26
	9	0.14	0	0	0	0.14
	12	0.14	0	0	0	0.14
	23	0.13	0	0	0	0.13
Solid	-1.5	8.18	0.27	0.07	0.58	9.1
	0	13.4	1.23	0.35	0.98	16
	1	13.4	0.91	0.25	0.97	15.6
	2	13.5	0.71	0.15	1	15.4
	4	11.9	0.52	0.08	0.87	13.4
	6	12.3	0.58	0.12	0.88	13.9
	9	12.4	0.53	0.07	0.89	13.9
	12	11.4	0.5	0.07	0.8	12.8
	23	9.27	0.38	0.08	0.66	10.4
EffAv	23.75	0.4	0	0	0	0.4
	Eff1	0.37	0	0	0	0.37
	Eff2	0.47	0	0	0	0.47
	Eff3	0.36	0	0	0	0.36
EffnextAv	23.75	0.413333	0	0	0	0.413333
	Effnext1	0.38	0	0	0	0.38
	Effnext2	0.43	0	0	0	0.43
	Effnext3	0.43	0	0	0	0.43

May 17, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.96	0.39	3.06	2.69	4.11
	Inf2	0.99	0.4	3.17	2.7	4.36
	Inf3	0.94	0.37	2.96	2.38	4.09
Liquid	-1.5	0	0	0	0	0
	0	0.29	0.12	0.75	0.56	1.79
	1	0.25	0.1	0.63	0.55	1.53
	2	0.25	0.09	0.59	0.48	1.43
	4	0.26	0.08	0.54	0.4	1.23
	6	0.28	0.08	0.5	0.26	1.06
	9	0.21	0	0.32	0.12	0.44
	12	0.22	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	0	0	0	0	0
	0	0.23	0	0.67	0.43	0.31
	1	0.24	0	0.66	0.44	0.34
	2	0.26	0	0.63	0.39	0.31
	4	0.28	0	0.58	0.31	0.25
	6	0.33	0	0.64	0.35	0.25
	9	0.27	0	0.45	0.3	0.15
	12	0.21	0	0	0.27	0
	23	0	0	0	0.14	0
EffAv	23.75	0	0	0	0	0
	Eff1	0	0	0	0	0
	Eff2	0	0	0	0	0
	Eff3	0	0	0	0	0
EffnextAv	23.75	0	0	0	0	0
	Effnext1	0	0	0	0	0
	Effnext2	0	0	0	0	0
	Effnext3	0	0	0	0	0

May 17, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	2.31	0.8	14.3	27.4
	Inf2	2.19	0.81	14.6	28.3
	Inf3	2.15	0.62	13.5	27
Liquid	-1.5	0	0	0	0.14
	0	0.44	0	3.96	4.94
	1	0.47	0.09	3.63	4.15
	2	0.4	0.09	3.32	3.71
	4	0.3	0.09	2.89	3.2
	6	0.19	0	2.36	2.62
	9	0	0.05	1.15	1.29
	12	0	0	0.22	0.35
	23	0	0	0	0.13
Solid	-1.5	0	0	0	9.1
	0	0.24	0	1.85	17.8
	1	0.24	0	1.92	17.5
	2	0.27	0	1.86	17.3
	4	0.22	0	1.65	15
	6	0.16	0.05	1.78	15.7
	9	0.16	0	1.33	15.2
	12	0	0	0.48	13.3
	23	0	0	0.14	10.5
EffAv	23.75	0	0	0	0.4
	Eff1	0	0	0	0.37
	Eff2	0	0	0	0.47
	Eff3	0	0	0	0.36
EffnextAv	23.75	0	0	0	0.413333
	Effnext1	0	0	0	0.38
	Effnext2	0	0	0	0.43
	Effnext3	0	0	0	0.43



May 24, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	6.65	5.01	1.12	0.44	13.2
	Inf2	6.6	5	1.11	0.42	13.1
	Inf3	6.28	5.2	1.3	0.49	13.3
Liquid	-1.5	0.14	0	0	0	0.14
	0	0.73	0.07	0	0.07	0.86
	1	0.58	0	0	0	0.58
	2	0.55	0	0	0.06	0.61
	4	0.36	0	0	0	0.36
	6	0.37	0	0	0	0.37
	9	0.31	0	0	0	0.31
	12	0.17	0	0	0	0.17
	23	0.17	0	0	0	0.17
Solid	-1.5	7.66	0.28	0.23	0.53	8.7
	0	9.82	0.49	0.27	0.71	11.3
	1	10.6	0.46	0.22	0.73	12
	2	10.8	0.45	0.21	0.77	12.2
	4	10.9	0.46	0.17	0.8	12.3
	6	11.3	0.43	0.08	0.76	12.5
	9	11.5	0.45	0.1	0.78	12.8
	12	10.6	0.41	0.14	0.72	11.8
	23	8.55	0.33	0.11	0.57	9.57
Storage	23.75	0.943333	5.01	4.373333	0.563333	10.9
	Storage1	0.94	4.95	4.38	0.55	10.8
	Storage2	0.93	4.89	4.3	0.53	10.7
	Storage3	0.96	5.19	4.44	0.61	11.2
EffAv	23.75	0.323333	0	0	0	0.323333
	Eff1	0.27	0	0	0	0.27
	Eff2	0.35	0	0	0	0.35
	Eff3	0.35	0	0	0	0.35
EffnextAv	23.75	0.37	0	0	0	0.37
	Effnext1	0.36	0	0	0	0.36
	Effnext2	0.39	0	0	0	0.39
	Effnext3	0.36	0	0	0	0.36

May 24, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.77	0.31	2.11	1.99	3.71
	Inf2	0.76	0.32	2.16	2.06	3.68
	Inf3	0.76	0.33	2.19	2.22	3.74
Liquid	-1.5	0	0	0	0	0
	0	0.18	0.08	0.45	0.43	1.4
	1	0.17	0	0.41	0.37	1.33
	2	0.18	0	0.41	0.37	1.24
	4	0.18	0	0.39	0.32	1.06
	6	0.2	0	0.39	0.28	0.95
	9	0.22	0	0.37	0.19	0.66
	12	0.09	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	0	0	0	0.13	0
	0	0.19	0	0.48	0.36	0.28
	1	0.21	0	0.49	0.37	0.29
	2	0.22	0	0.51	0.37	0.29
	4	0.25	0	0.52	0.37	0.3
	6	0.28	0	0.52	0.36	0.26
	9	0.3	0	0.47	0.33	0.17
	12	0.15	0	0	0.23	0.09
	23	0	0	0	0.14	0
Storage	23.75	2.946667	1.76	7.433333	9.833333	12.66667
	Storage1	3.07	1.4	7.77	10.3	13.7
	Storage2	2.87	1.77	7.28	9.4	12.4
	Storage3	2.9	2.11	7.25	9.8	11.9
EffAv	23.75	0	0	0	0	0
	Eff1	0	0	0	0	0
	Eff2	0	0	0	0	0
	Eff3	0	0	0	0	0
EffnextAv	23.75	0	0	0	0	0
	Effnext1	0	0	0	0	0
	Effnext2	0	0	0	0	0
	Effnext3	0	0	0	0	0

May 24, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	2.1	0.54	11.5	24.8
	Inf2	2.04	0.52	11.5	24.7
	Inf3	1.99	0.44	11.7	24.9
Liquid	-1.5	0	0	0	0.14
	0	0.41	0	2.96	3.82
	1	0.32	0	2.6	3.18
	2	0.34	0	2.53	3.15
	4	0.24	0.08	2.26	2.62
	6	0.18	0	2.01	2.38
	9	0.09	0	1.52	1.83
	12	0	0	0.09	0.26
	23	0	0	0	0.17
Solid	-1.5	0	0	0.13	8.83
	0	0.37	0	1.69	13
	1	0.35	0	1.7	13.7
	2	0.28	0.07	1.75	14
	4	0.23	0.12	1.81	14.1
	6	0.16	0.23	1.81	14.3
	9	0.09	0	1.36	14.2
	12	0	0	0.47	12.3
	23	0	0	0.14	9.7
Storage	23.75	9.523333	3.206667	47.36667	58.3
	Storage1	9.65	3.31	49.1	60
	Storage2	9.4	3.06	46.2	56.9
	Storage3	9.52	3.25	46.8	58
EffAv	23.75	0	0	0	0.323333
	Eff1	0	0	0	0.27
	Eff2	0	0	0	0.35
	Eff3	0	0	0	0.35
EffnextAv	23.75	0	0	0	0.37
	Effnext1	0	0	0	0.36
	Effnext2	0	0	0	0.39
	Effnext3	0	0	0	0.36

June 7, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	7.82	9.31	2.4	0.62	20.14
	Inf2	7.97	9.41	2.47	0.75	20.6
	Inf3	8.29	9.15	2.13	0.43	20
Liquid	-1.5	0.46	0	0	0	0.46
	0	1.04	0.09	0	0	1.13
	1	0.81	0	0	0	0.81
	2	1.09	0	0	0	1.09
	4	1.02	0	0	0	1.02
	6	1.41	0	0	0	1.41
	9	1.41	0	0	0	1.41
	12	1.39	0	0	0	1.39
	23	0.35	0	0	0	0.35
Solid	-1.5	5.64	0.21	0	0.29	6.14
	0	11.4	0.66	0.16	0.74	13
	1	11.5	0.52	0.13	0.76	12.9
	2	11.6	0.52	0.15	0.83	13.1
	4	10	0.43	0.11	0.66	11.2
	6	9.54	0.38	0.09	0.59	10.6
	9	9.19	0.35	0	0.53	10.1
	12	7.92	0.33	0	0.52	8.77
	23	6.5	0.27	0	0.36	7.13
	Eff1	1.55	0	0	0	1.55
	Eff2	1.41	0	0	0	1.41
	Eff3	1.39	0	0	0	1.39
	Storage	1.73	9.83	8.41	0.31	20.3

June 7, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	1.13	0.48	3.09	3.16	4.86
	Inf2	1.13	0.47	3	2.72	4.7
	Inf3	1.14	0.48	3.17	3.23	5.12
Liquid	-1.5	0	0	0	0	0
	0	0.26	0	0.63	0.68	1.83
	1	0.24	0	0.6	0.7	1.82
	2	0.24	0	0.61	0.7	1.68
	4	0.25	0	0.6	0.61	1.6
	6	0.26	0	0.63	0.62	1.55
	9	0.28	0	0.65	0.57	1.55
	12	0.29	0	0.54	0.27	0.72
	23	0	0	0	0	0
Solid	-1.5	0	0	0	0	0
	0	0.29	0	0.76	0.64	0.6
	1	0.3	0.11	0.73	0.58	0.56
	2	0.32	0	0.79	0.58	0.58
	4	0.37	0.11	0.9	0.67	0.6
	6	0.34	0	0.78	0.5	0.52
	9	0.35	0	0.76	0.45	0.49
	12	0.38	0	0.64	0.31	0.26
	23	0	0	0	0	0
	Eff1	0	0	0	0	0
	Eff2	0	0	0	0	0
	Eff3	0	0	0	0	0
Storage		5.56	2.73	14.3	20.4	21.7

June 7, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	3.09	0.83	16.6	36.8
	Inf2	3.11	0.77	15.9	36.5
	Inf3	3.15	0.77	17.1	37.1
Liquid	-1.5	0	0	0	0.46
	0	0.69	0.16	4.23	5.36
	1	0.67	0.17	4.2	5.01
	2	0.65	0.17	4.06	5.15
	4	0.52	0	3.58	4.6
	6	0.51	0.16	3.73	5.14
	9	0.41	0	3.45	4.87
	12	0	0	1.82	3.21
	23	0	0	0	0.35
Solid	-1.5	0	0	0	6.14
	0	0.56	0.17	3.03	16
	1	0.58	0.16	3.03	16
	2	0.57	0.17	3.01	16.1
	4	0.56	0.2	3.39	14.6
	6	0.43	0.15	2.71	13.3
	9	0.36	0	2.4	12.5
	12	0.12	0	1.71	10.5
	23	0	0	0	7.13
	Eff1	0	0	0	1.55
	Eff2	0	0	0	1.41
	Eff3	0	0	0	1.39
	Storage	18.5	6.88	90.1	110.4

June 16, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	8.67	6	1.28	0.45	16.4
	Inf2	9.75	6.36	1.38	0.56	18.1
	Inf3	9.66	6.36	1.39	0.51	17.9
Liquid	-1.5	0.19	0	0	0	0.19
	0	0.32	0	0	0	0.32
	1	0.35	0	0	0	0.35
	2	0.31	0	0	0	0.31
	4	0.59	0	0	0	0.59
	6	0.56	0	0	0	0.56
	9	0.6	0	0	0	0.6
	12	0.67	0	0	0	0.67
	23	0.25	0	0	0	0.25
Solid	-1.5	6.47	0.21	0.09	0.41	7.17
	0	10.3	0.54	0.17	0.75	11.8
	1	10.8	0.44	0.13	0.8	12.2
	2	10.4	0.42	0.13	0.77	11.7
	4	10.2	0.4	0.13	0.72	11.4
	6	11.1	0.44	0.14	0.84	12.5
	9	10.6	0.38	0.11	0.72	11.9
	12	9.89	0.39	0.14	0.69	11.1
	23	7.55	0.3	0.12	0.49	8.46
	Eff1	0.87	0	0	0	0.87
	Eff2	0.82	0	0	0	0.82
	Eff3	0.85	0	0	0	0.85
Storage		1.1	6.14	5.19	0.38	12.8

June 16, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	1	0.42	3.37	2.62	4.14
	Inf2	1.05	0.45	3.51	2.67	4.34
	Inf3	1.06	0.47	3.54	2.62	4.44
Liquid	-1.5	0	0	0	0	0
	0	0.2	0.08	0.59	0.46	1.41
	1	0.16	0.06	0.44	0.39	1.1
	2	0.16	0.06	0.45	0.39	1.12
	4	0.18	0.06	0.44	0.37	1.1
	6	0.2	0.07	0.46	0.36	1.07
	9	0.19	0.06	0.4	0.34	0.89
	12	0.21	0	0.29	0	0.13
	23	0	0	0	0	0
Solid	-1.5	0	0	0	0.09	0
	0	0.24	0.09	0.68	0.35	0.47
	1	0.26	0.09	0.7	0.33	0.56
	2	0.27	0.09	0.69	0.33	0.51
	4	0.28	0.09	0.67	0.31	0.5
	6	0.32	0.09	0.7	0.31	0.39
	9	0.32	0.08	0.63	0.28	0.37
	12	0.37	0	0.47	0.25	0.14
	23	0	0	0	0.13	0
	Eff1	0	0	0	0	0
	Eff2	0	0	0	0	0
	Eff3	0	0	0	0	0
	Storage	3.72	2.93	9.53	13.5	15



June 16, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	2.28	0.68	14.5	30.9
	Inf2	2.33	0.68	15	33.1
	Inf3	2.32	0.63	15.1	33
Liquid	-1.5	0	0	0	0.19
	0	0.45	0	3.2	3.52
	1	0.36	0.08	2.59	2.93
	2	0.36	0	2.55	2.86
	4	0.35	0.07	2.58	3.17
	6	0.29	0	2.44	3
	9	0.24	0.07	2.19	2.79
	12	0	0	0.62	1.29
	23	0	0	0	0.25
Solid	-1.5	0	0	0.09	7.27
	0	0.33	0	2.16	13.9
	1	0.36	0	2.29	14.5
	2	0.36	0.08	2.32	14
	4	0.32	0	2.17	13.6
	6	0.31	0	2.12	14.7
	9	0.22	0	1.9	13.8
	12	0	0	1.23	12.4
	23	0	0	0.13	8.58
	Eff1	0	0	0	0.87
	Eff2	0	0	0	0.82
	Eff3	0	0	0	0.85
Storage		12.6	4.57	61.9	74.7

June 26, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	3.1	1.41	0.39	0.21	5.11
	Inf2	3.06	1.52	0.46	0.26	5.31
	Inf3	2.71	1.42	0.4	0.14	4.67
Liquid	-1.5	0.06	0	0	0	0.06
	0	0.25	0	0	0	0.25
	1	0.09	0	0	0	0.09
	2	0.08	0	0	0	0.08
	4	0.08	0	0	0	0.08
	6	0.07	0	0	0	0.07
	9	0.05	0	0	0	0.05
	12	0	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	2.58	0.2	0.1	0.27	3.16
	0	3.36	0.23	0.09	0.32	4
	1	3.38	0.23	0.09	0.31	4.01
	2	3.34	0.23	0.09	0.32	3.95
	4	3.48	0.22	0.07	0.31	4.08
	6	3.51	0.24	0.1	0.34	4.19
	9	3.29	0.27	0.12	0.37	4.05
	12	3	0.23	0.09	0.32	3.64
	23	2.51	0.23	0.11	0.31	3.16
	Eff	0.44	0	0	0	0.44

June 26, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.47	0.21	1.26	1.2	2.98
	Inf2	0.48	0.21	1.26	1.2	3
	Inf3	0.46	0.2	1.21	1.22	2.88
Liquid	-1.5	0	0	0	0.13	1.04
	0	0.11	0	0.34	0.43	1.59
	1	0.11	0	0.36	0.39	1.7
	2	0.12	0	0.38	0.43	1.78
	4	0.09	0	0.35	0.32	1.84
	6	0	0	0.31	0.32	1.81
	9	0	0	0.24	0.2	1.68
	12	0	0	0	0	1.42
	23	0	0	0	0	0.91
	-1.5	0	0	0.3	0.13	0.4
Solid	0	0.18	0	0.54	0.24	0.59
	1	0.19	0	0.54	0.25	0.6
	2	0.19	0	0.58	0.25	0.65
	4	0.19	0	0.62	0.23	0.77
	6	0.15	0	0.54	0.27	0.71
	9	0.14	0	0.43	0.27	0.63
	12	0	0	0.33	0.23	0.57
	23	0	0	0	0.14	0.43
	Eff	0	0	0	0.12	0.98

June 26, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	1.32	0.31	7.76	12.9
	Inf2	1.32	0.29	7.76	13.1
	Inf3	1.34	0.36	7.68	12.3
Liquid	-1.5	0	0.31	1.47	1.53
	0	0.38	0.23	3.08	3.34
	1	0.36	0.18	3.09	3.18
	2	0.38	0.21	3.3	3.38
	4	0.29	0.23	3.12	3.2
	6	0.31	0.31	3.06	3.12
	9	0.19	0.34	2.65	2.7
	12	0	0.35	1.77	1.77
	23	0	0.35	1.26	1.26
Solid	-1.5	0.18	0.16	1.18	4.34
	0	0.4	0.13	2.09	6.09
	1	0.42	0.14	2.14	6.15
	2	0.42	0.12	2.21	6.17
	4	0.43	0.15	2.39	6.48
	6	0.39	0.19	2.24	6.44
	9	0.35	0.2	2.02	6.06
	12	0.29	0.21	1.63	5.27
	23	0.16	0.19	0.91	4.07
	Eff	0	0.33	1.43	1.87

July 5, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	8.58	4.01	1.73	0.54	14.86
	Inf2	9.03	4.08	1.78	0.56	15.45
	Inf3	8.87	4.27	1.79	0.55	15.48
Liquid	-1.5	0.05	0	0	0	0.05
	0	0.55	0	0	0	0.55
	1	0.41	0	0	0	0.41
	2	0.31	0	0	0	0.31
	4	0.23	0	0	0	0.23
	6	0.13	0	0	0	0.13
	9	0.14	0	0	0	0.14
	12	0.12	0	0	0	0.12
	23	0	0	0	0	0
Solid	-1.5	3.66	0.3	0.16	0.36	4.48
	0	7.69	0.73	0.32	0.76	9.49
	1	7.97	0.64	0.25	0.72	9.58
	2	7.17	0.54	0.21	0.74	8.65
	4	6.25	0.43	0.16	0.61	7.45
	6	5.75	0.47	0.16	0.61	6.99
	9	4.75	0.39	0.13	0.48	5.75
	12	4.12	0.37	0.13	0.46	5.08
	23	3.02	0.36	0.16	0.34	3.88
	Eff	0.79	0.07	0	0.07	0.93
	Storage	1.11	6.92	5.59	0.76	14.38

July 5, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+Lev	DHA
	Inf1	1.28	0.74	4.21	5.18	6.58
	Inf2	1.39	0.95	4.3	5.28	6.99
	Inf3	1.29	1.36	4.2	5.4	6.88
Liquid	-1.5	0	0	0.25	0.17	1.38
	0	0.3	0.12	0.97	1.03	2.72
	1	0.28	0.11	0.87	0.89	2.62
	2	0.31	0.13	0.98	1.04	2.75
	4	0.31	0.11	0.99	1.03	2.83
	6	0.3	0.15	0.88	1.06	2.57
	9	0.32	0.15	0.93	1.03	2.66
	12	0.31	0.11	0.91	0.98	2.66
	23	0.15	0	0.83	0.75	2.71
Solid	-1.5	0.24	0	0.48	0.28	0.58
	0	0.6	0.22	1.75	1.02	1.27
	1	0.74	0.27	1.78	1.15	1.13
	2	0.84	0.35	1.85	1.04	1.28
	4	0.6	0.19	1.73	0.87	1.22
	6	0.62	0.17	1.72	0.72	1.24
	9	0.67	0.16	1.8	0.73	1.18
	12	0.65	0.17	1.83	0.69	1.24
	23	0.39	0	1.51	0.45	1.2
Eff		0	0	0.25	0.24	1.22
Storage		3.34	2.53	9.94	16.67	14.21

July 5, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	3.17	1.15	22.32	37.18
	Inf2	3.23	1.11	23.25	38.7
	Inf3	3.04	1.04	23.2	38.69
Liquid	-1.5	0.11	0.27	2.28	2.33
	0	0.77	0.43	6.34	6.89
	1	0.77	-0.48	6.02	6.43
	2	0.89	0.51	6.61	6.92
	4	0.92	0.53	6.73	6.95
	6	0.89	0.52	6.36	6.49
	9	0.87	0.48	6.44	6.58
	12	0.81	0.49	6.27	6.39
	23	0.64	0.61	5.69	5.69
Solid	-1.5	0.34	0.31	2.23	6.7
	0	1.02	0.33	6.22	15.71
	1	1.17	0.5	6.73	16.31
	2	1.19	0.49	7.04	15.69
	4	1.12	0.45	6.18	13.62
	6	1.15	0.44	6.05	13.05
	9	1.13	0.45	6.13	11.88
	12	1.12	0.42	6.21	11.2
	23	0.87	0.36	4.77	8.65
	Eff	0.22	0.5	2.42	3.35
	Storage	13.61	5.35	66.26	80.63

July 12, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	1.45	0.43	0.12	0.21	2.22
	Inf2	1.48	0.4	0.11	0.12	2.12
	Inf3	1.49	0.42	0.13	0.13	2.17
Liquid	-1.5	0	0	0	0	0
	0	0.11	0	0	0	0.11
	1	0.04	0	0	0	0.04
	2	0	0	0	0	0
	4	0	0	0	0	0
	6	0	0	0	0	0
	9	0	0	0	0	0
	12	0	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	1.01	0.33	0.16	0.32	1.82
	0	1.44	0.32	0.14	0.26	2.17
	1	1.42	0.32	0.15	0.34	2.24
	2	1.45	0.35	0.16	0.34	2.3
	4	1.29	0.36	0.16	0.33	2.15
	6	1.28	0.36	0.17	0.34	2.15
	9	1.04	0.35	0.16	0.31	1.86
	12	0.87	0.28	0.15	0.37	1.66
	23	0.99	0.31	0.16	0.29	1.76
	Eff	0.07	0	0	0	0.07
	Storage	0.74	3.96	3.52	0.49	8.71



July 12, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.22	0.11	0.57	0.62	2.02
	Inf2	0.23	0.19	0.62	0.66	2.13
	Inf3	0.25	0.13	0.62	0.69	2.17
Liquid	-1.5	0	0	0.34	0.4	2.26
	0	0.11	0	0.38	0.42	2.12
	1	0.09	0	0.39	0.49	2.02
	2	0.09	0	0.38	0.43	2.12
	4	0.1	0	0.37	0.42	2.06
	6	0.12	0	0.36	0.48	2.07
	9	0.07	0	0.35	0.38	2.15
	12	0.07	0	0.33	0.37	2.13
	23	0.08	0	0.32	0.34	0.32
Solid	-1.5	0.27	0	0.44	0.21	0.65
	0	0.32	0	0.55	0.28	0.71
	1	0.35	0	0.59	0.27	0.76
	2	0.29	0	0.59	0.27	0.79
	4	0.35	0	0.5	0.22	0.66
	6	0.28	0	0.53	0.25	0.69
	9	0.28	0	0.52	0.25	0.77
	12	0.26	0	0.44	0.22	0.69
	23	0.23	0	0.39	0.19	0.67
	Eff	0	0	0.3	0.33	1.96
	Storage	2.62	1.76	6.52	9.59	10.2

July 12, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	0.58	0.15	4.29	6.51
	Inf2	0.59	0.12	4.53	6.65
	Inf3	0.59	0.13	4.58	6.75
Liquid	-1.5	0.39	0.68	4.08	4.08
	0	0.41	0.45	3.89	4
	1	0.5	0.47	3.97	4
	2	0.42	0.47	3.92	3.92
	4	0.42	0.45	3.81	3.81
	6	0.5	0.55	4.08	4.08
	9	0.42	0.49	3.86	3.86
	12	0.37	0.48	3.75	3.75
	23	0.34	0.55	3.94	3.94
Solid	-1.5	0.43	0.33	2.34	4.15
	0	0.52	0.22	2.6	4.76
	1	0.54	0.23	2.75	4.98
	2	0.54	0.25	2.73	5.03
	4	0.48	0.2	2.42	4.57
	6	0.5	0.21	2.46	4.61
	9	0.51	0.22	2.54	4.4
	12	0.4	0.19	2.2	3.86
	23	0.41	0.17	2.07	3.83
	Eff	0.36	0.66	3.61	3.68
	Storage	8.49	2.77	41.9	50.6

July 19, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	6.69	2.65	0.62	0.42	10.4
	Inf2	7	2.98	0.8	0.46	11.2
	Inf3	7.05	2.9	0.77	0.44	11.1
Liquid	-1.5	0	0	0	0	0
	0	0.53	0.14	0	0	0.67
	1	0.36	0.12	0	0	0.48
	2	0.17	0	0	0	0.17
	4	0.11	0	0	0	0.11
	6	0.09	0	0	0	0.09
	9	0.06	0	0	0	0.06
	12	0.05	0	0	0	0.05
	18	0.04	0	0	0	0.04
	23	0	0	0	0	0
Solid	-1.5	2.42	0.32	0.18	0.44	3.36
	0	5.79	0.91	0.36	0.62	7.68
	1	5.86	0.91	0.41	0.71	7.88
	2	5.66	0.7	0.34	0.64	7.33
	4	5.36	0.53	0.25	0.64	6.79
	6	4.79	0.46	0.22	0.67	6.15
	9	4.36	0.46	0.21	0.65	5.68
	12	3.9	0.41	0.17	0.48	4.97
	18	2.79	0.39	0.16	0.44	3.78
	23	2.3	0.35	0.15	0.33	3.13
	Eff	0.51	0	0	0	0.51
	Effnext	0.4	0	0	0	0.4
	Storage	1.65	7.66	9.07	0.49	18.9

July 19, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.63	0.26	2.07	2.01	3.57
	Inf2	0.62	0.25	2.1	2.01	3.7
	Inf3	0.63	0.25	2.02	1.89	3.57
Liquid	-1.5	0.3	0.11	1.25	0.79	3.48
	0	0.4	0.16	1.54	1.15	3.57
	1	0.4	0.15	1.51	1.02	3.67
	2	0.34	0.17	1.26	0.88	3.06
	4	0.36	0.14	1.42	0.89	3.51
	6	0.34	0.13	1.42	0.77	3.41
	9	0.33	0.12	1.31	0.81	3.22
	12	0.33	0.13	1.38	0.71	3.56
	18	0.36	0.12	1.56	0.8	3.79
	23	0.33	0.1	1.37	0.78	3.47
Solid	-1.5	0.4	0.11	1.53	0.33	1.05
	0	0.52	0.17	1.67	0.74	0.99
	1	0.43	0.15	1.56	0.76	0.97
	2	0.46	0.15	1.62	0.75	0.98
	4	0.43	0.14	1.6	0.64	0.91
	6	0.44	0.13	1.67	0.59	0.97
	9	0.48	0.15	1.79	0.6	1.28
	12	0.46	0.15	1.81	0.57	1.04
	18	0.48	0.13	1.81	0.37	1.07
	23	0.45	0.13	1.83	0.57	1.06
	Eff	0.29	0	1.02	0.52	3.12
	Effnext	0.31	0.12	1.27	0.62	3.72
	Storage	5.16	1.82	13	16.7	18.5

July 19, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	1.23	0.38	10.1	20.5
	Inf2	1.22	0.3	10.2	21.4
	Inf3	1.21	0.34	9.89	21.1
Liquid	-1.5	0.97	0.38	7.28	7.28
	0	1.07	0.3	8.17	8.84
	1	0.88	0.27	7.91	8.39
	2	1.06	0.34	7.12	7.29
	4	0.87	0.28	7.47	7.58
	6	0.76	0.2	7.02	7.11
	9	1.03	0.24	7.05	7.11
	12	0.73	0.21	7.04	7.09
	18	0.86	0.19	7.68	7.72
	23	0.93	0.23	7.22	7.22
Solid	-1.5	0.57	0.1	4.08	7.44
	0	0.78	0.22	5.09	12.8
	1	0.74	0.15	4.75	12.6
	2	0.71	0.12	4.8	12.1
	4	0.71	0.17	4.6	11.4
	6	0.7	0.15	4.66	10.8
	9	0.76	0.13	5.17	10.8
	12	0.76	0.15	4.94	9.91
	18	0.73	0.11	4.71	8.49
	23	0.73	1.08	4.88	8.01
	Eff	0.82	0.27	6.03	6.55
	Effnext	0.73	0.23	7.01	7.4
	Storage	15.9	5.06	76.1	95

July 29, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	2.44	1.34	0.45	0.19	4.42
	Inf2	2.42	1.33	0.45	0.17	4.37
	Inf3	2.87	1.6	0.52	0.42	5.41
Liquid	-1.5	0	0	0	0	0
	0	0.12	0	0	0	0.12
	1	0.05	0	0	0	0.05
	2	0	0	0	0	0
	4	0	0	0	0	0
	6	0	0	0	0	0
	9	0	0	0	0	0
	12	0	0	0	0	0
	18	0	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	0.63	0.22	0.14	0.19	1.18
	0	1.39	0.28	0.15	0.31	2.13
	1	1.13	0.23	0.13	0.3	1.8
	2	1.08	0.41	0.18	0.25	1.91
	4	1.05	0.37	0.17	0.25	1.84
	6	0.9	0.27	0.13	0.25	1.55
	9	0.95	0.36	0.15	0.22	1.69
	12	0.63	0.21	0.1	0.15	1.11
	18	0.72	0.25	0.13	0.27	1.36
	23	0.71	0.24	0.12	0.19	1.26
	Eff	0.08	0	0	0	0.08
	Store Old	0.95	4.81	4.46	0.31	10.5
	Store New	1.57	6.72	8.88	0.49	17.6

July 29, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.54	0.22	1.92	0.75	3.67
	Inf2	0.55	0.22	1.91	0.68	3.6
	Inf3	0.6	0.24	2.2	0.76	3.98
Liquid	-1.5	0.23	0	1.2	0	3.56
	0	0.34	0.13	1.45	0.15	3.67
	1	0.33	0.12	1.58	0.22	3.51
	2	0	0	0	0	0
	4	0.25	0.09	1.14	0.12	3.19
	6	0.26	0.1	1.23	0.13	3.5
	9	0.26	0.1	1.24	0.14	3.48
	12	0.29	0.11	1.41	0	3.57
	18	0.3	0.11	1.56	0.14	3.85
	23	0.29	0.1	1.48	0.13	3.82
Solid	-1.5	0.27	0	1.33	0	1.2
	0	0.33	0.1	1.46	0.12	1.33
	1	0.42	0.14	1.4	0	1.14
	2	0.34	0.09	1.52	0	1.36
	4	0.45	0.17	1.91	0	1.48
	6	0.35	0.12	1.7	0	1.41
	9	0.39	0.13	1.9	0.11	1.32
	12	0.35	0.13	1.4	0	1.01
	18	0.31	0.1	1.47	0	1.19
	23	0.35	0.13	1.42	0	1.08
	Eff	0.24	0	1.18	0	3.35
	Store Old	3.32	2.71	8.19	5.04	18.5
	Store New	5.42	2.53	12.8	7.66	26.5

July 29, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	0.53	0	7.62	12
	Inf2	0.55	0	7.51	11.9
	Inf3	0.72	0	8.51	13.9
Liquid	-1.5	0.15	0.25	5.38	5.38
	0	0.2	0.15	6.19	6.21
	1	0.3	0.16	6.23	6.28
	2	0	0.15	0.15	0.15
	4	0.22	0.13	5.12	5.12
	6	0.22	0.17	5.61	5.61
	9	0.24	0.16	5.64	5.64
	12	0.24	0.2	5.82	5.82
	18	0.26	0.22	6.45	6.45
	23	0.24	0.26	6.32	6.32
Solid	-1.5	0.21	0	3.01	4.19
	0	0.27	0	3.62	5.75
	1	0.27	0	3.37	5.17
	2	0.33	0	3.63	5.54
	4	0.44	0	4.46	6.3
	6	0.41	0	3.99	5.53
	9	0.46	0	4.32	6
	12	0.29	0	3.19	4.3
	18	0.32	0	3.39	4.76
	23	0.27	0	3.25	4.51
	Eff	0.14	0.25	5.17	5.25
	Store Old	9.2	1.32	48.2	58.8
	Store New	13.4	1.76	70.1	87.7



August 15, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	1.03	1.67	0.49	0.16	3.34
	Inf2	1.05	1.61	0.44	0.07	3.17
	Inf3	1.04	1.54	0.44	0.15	3.17
Liquid	-1.5	0	0	0	0	0
	0	0.1	0	0	0	0.1
	1	0.07	0.08	0	0	0.15
	2	0.06	0	0	0	0.06
	4	0	0	0	0	0
	6	0	0	0	0	0
	9	0	0	0	0	0
	12	0	0	0	0	0
	18	0	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	0.6	0.31	0	0.19	1.1
	0	1.14	0.84	0.18	0.24	2.41
	1	1.01	0.71	0.14	0.21	2.07
	2	1.1	0.68	0.15	0.27	2.21
	4	0.97	0.52	0.1	0.26	1.85
	6	0.78	0.39	0	0.21	1.38
	9	0.68	0.38	0	0.19	1.24
	12	0.71	0.38	0	0.18	1.27
	18	0.68	0.37	0	0.24	1.28
	23	0.62	0.31	0	0.16	1.1
	Eff	0.08	0	0	0	0.08
	Store Old	1.84	10.8	8.69	0.35	21.7
	Store New	1.58	7.4	9.29	0.43	18.7

August 15, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.52	0.22	1.39	1.21	3.37
	Inf2	0.53	0.22	1.39	1.14	3.44
	Inf3	0.51	0.22	1.36	1.14	3.36
Liquid	-1.5	0.73	0.24	2.19	0.88	5.46
	0	0.79	0.27	2.47	1.23	4.98
	1	0.82	0.29	2.68	1.26	4.81
	2	0.83	0.29	2.74	1.25	5
	4	0.82	0.28	2.69	1.28	4.92
	6	0.82	0.29	2.71	1.13	5.12
	9	0.85	0.3	2.82	1.11	5.13
	12	0.79	0.24	2.59	1.12	5.13
	18	0.74	0.25	2.41	1.03	5.15
	23	0.76	0.25	2.46	0.87	5.33
Solid	-1.5	0.4	0.18	1.33	0.18	0.95
	0	0.45	0.21	1.68	0.28	1.28
	1	0.4	0.19	1.52	0.26	0.92
	2	0.42	0.21	1.63	0.24	0.98
	4	0.45	0.21	1.62	0.28	1.12
	6	0.43	0.2	1.61	0.22	1.26
	9	0.39	0.19	1.55	0.21	0.99
	12	0.4	0.19	1.57	0.25	0.96
	18	0.41	0.19	1.62	0.21	1.27
	23	0.4	0.18	1.56	0.24	1.19
	Eff	0.59	0.2	1.71	0.67	4.96
	Store Old	6.24	2.91	16	22.1	25.6
	Store New	5.29	1.78	12.5	14.6	20.9

August 15, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	1.5	0.34	8.54	11.9
	Inf2	1.47	0.31	8.49	11.7
	Inf3	1.44	0.34	8.38	11.6
Liquid	-1.5	1.1	0.16	10.8	10.8
	0	1.46	0.21	11.4	11.5
	1	1.54	0.19	11.6	11.7
	2	1.49	0	11.6	11.7
	4	1.56	0.2	11.8	11.8
	6	1.31	0	11.4	11.4
	9	1.35	0	11.6	11.6
	12	1.38	0.17	11.4	11.4
	18	1.26	0.2	11	11
	23	1.11	0.17	10.9	10.9
Solid	-1.5	0.47	0	3.52	4.62
	0	0.67	0	4.57	6.98
	1	0.66	0	3.95	6.02
	2	0.58	0	4.06	6.27
	4	0.67	0	4.34	6.2
	6	0.61	0	4.33	5.7
	9	0.58	0	3.92	5.16
	12	0.54	0	3.9	5.17
	18	0.6	0	4.3	5.58
	23	0.54	0	4.11	5.21
	Eff	0.9	0.18	9.22	9.3
	Store Old	21.3	7.37	102	123
	Store New	14.9	4.47	74.4	93.1

August 22, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	1.27	2.41	0.79	0.16	4.63
	Inf2	1.33	2.51	0.82	0.12	4.77
	Inf3	1.36	2.58	0.85	0.21	5.01
Liquid	-1.5	0	0	0	0	0
	0	0.09	0.09	0	0	0.18
	1	0.07	0.07	0	0	0.14
	2	0.08	0	0	0	0.08
	4	0.05	0	0	0	0.05
	6	0	0	0	0	0
	9	0	0	0	0	0
	12	0	0	0	0	0
	18	0	0	0	0	0
	23	0	0	0	0	0
Solid	-1.5	0.37	0.23	0	0	0.6
	0	0.61	0.53	0.11	0	1.26
	1	0.6	0.5	0.11	0.12	1.33
	2	0.58	0.44	0.1	0.13	1.26
	4	0.5	0.3	0.07	0.11	0.99
	6	0.45	0.25	0	0.13	0.84
	9	0.54	0.32	0	0.21	1.06
	12	0.41	0.22	0	0	0.63
	18	0.41	0.22	0	0	0.63
	23	0.47	0.25	0	0	0.72
	Eff	0.08	0.22	0	0	0.3
	Store Old	1.35	7.87	6.31	0.42	15.9
	Store New	1.13	0.52	6.44	0.29	8.38

August 22, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.64	0.26	1.74	1.04	3.7
	Inf2	0.66	0.27	1.95	1.35	4.01
	Inf3	0.67	0.28	1.89	1.33	3.81
Liquid	-1.5	0.63	0.2	2.12	0.49	4.14
	0	0.53	0.18	1.77	0.61	3.4
	1	0.55	0.19	1.87	0.58	3.48
	2	0.57	0.18	1.92	0.48	3.58
	4	0.55	0.19	1.91	0.62	3.41
	6	0.55	0.18	1.86	0.51	3.59
	9	0.58	0.19	1.96	0.48	3.78
	12	0.56	0.18	1.95	0.49	3.65
	18	0.57	0.17	1.96	0.27	3.8
	23	0.59	0.19	2.01	0.39	3.99
Solid	-1.5	0.33	0.15	1.26	0	0.64
	0	0.3	0.14	1.18	0.24	0.73
	1	0.34	0.16	1.27	0.22	0.71
	2	0.28	0.14	1.25	0.22	0.72
	4	0.33	0.16	1.23	0.19	0.7
	6	0.33	0.16	1.33	0.18	0.64
	9	0.36	0.18	1.38	0.13	0.93
	12	0.3	0	1.28	0	0.64
	18	0.3	0.14	1.23	0	0.64
	23	0.3	0	1.33	0	0.69
	Eff	0.52	0.17	1.62	0.26	3.82
	Store Old	4.59	2.18	11.8	16.1	18.6
	Store New	3.59	1.24	8.64	10.4	12.8

August 22, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	1.5	0.19	9.08	13.7
	Inf2	1.64	0.22	10.1	14.9
	Inf3	1.7	0.26	9.95	15
Liquid	-1.5	0.61	0.17	8.36	8.36
	0	0.77	0.14	7.4	7.58
	1	0.71	0	7.38	7.52
	2	0.66	0	7.38	7.46
	4	0.8	0.13	7.61	7.66
	6	0.66	0	7.36	7.36
	9	0.64	0.15	7.78	7.78
	12	0.68	0.14	7.66	7.66
	18	0.46	0.13	7.35	7.35
	23	0.55	0.19	7.9	7.9
Solid	-1.5	0.34	0	2.73	3.33
	0	0.4	0	2.98	4.24
	1	0.42	0	3.11	4.45
	2	0.42	0	3.03	4.29
	4	0.39	0	3.01	4
	6	0.42	0	3.05	3.9
	9	0.37	0	3.35	4.41
	12	0.34	0	2.56	3.19
	18	0.3	0	2.61	3.25
	23	0.34	0	2.66	3.38
	Eff	0.44	0.13	6.96	7.26
	Store Old	15.3	4.94	73.3	89.2
	Store New	10.8	3.35	50.9	59.3

September 6, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	0.76	0.23	0.12	0.13	1.24
	Inf2	0.51	0.16	0.09	0.07	0.84
	Inf3	0.7	0.21	0.12	0.11	1.14
Liquid	-1.5	0.1	0	0	0	0.1
	0	0.18	0	0	0	0.18
	1	0.17	0.07	0	0.11	0.35
	2	0.08	0	0	0	0.08
	4	0.09	0	0	0	0.09
	6	0.08	0	0	0	0.08
	9	0	0	0	0	0
	12	0	0	0	0	0
	18	0.07	0	0	0	0.07
	23	0.09	0	0	0	0.09
Solid	-1.5	0.5	0.1	0	0.12	0.72
	0	0.68	0.2	0.08	0.17	1.13
	1	0.64	0.23	0.09	0.25	1.22
	2	0.58	0.16	0	0.12	0.86
	4	0.54	0.13	0	0.14	0.81
	6	0.49	0.13	0	0.14	0.76
	9	0.45	0.13	0	0.14	0.72
	12	0.44	0.11	0	0.11	0.55
	18	0.33	0	0	0	0.33
	23	0.36	0.08	0	0.09	0.53
	Eff	0.19	0	0	0	0.19

September 6, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.99	0.15	1.01	0.5	3.9
	Inf2	0.29	0.11	0.71	0.38	2.65
	Inf3	0.78	0.15	0.94	0.53	3.57
Liquid	-1.5	0.62	0.17	1.8	0	4.23
	0	0.6	0.12	1.27	0.17	3.04
	1	0.72	0.17	1.57	0.18	3.75
	2	0.43	0.14	1.41	0.19	3.23
	4	0.52	0.16	1.63	0.21	3.78
	6	0.53	0.17	1.66	0.24	3.68
	9	0.4	0.13	1.31	0.16	2.85
	12	0.44	0.13	1.28	0.15	2.95
	18	0.45	0.15	1.5	0	3.42
	23	0.57	0.18	1.78	0.19	4.26
Solid	-1.5	0.44	0.11	1.29	0	1.22
	0	0.34	0.11	1.21	0	1.02
	1	0.7	0.11	1.07	0	0.78
	2	0.31	0.12	1.12	0	0.7
	4	0.34	0.13	1.17	0	0.89
	6	0.35	0.12	1.18	0	0.93
	9	0.33	0.1	1.07	0	0.9
	12	0.32	0.11	1.08	0	0.98
	18	0.32	0	0.94	0	0.66
	23	0.38	0.12	1.15	0	0.83
	Eff	0.69	0.18	1.84	0	4.42



September 6, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	0.95	0	7.49	8.73
	Inf2	0.67	0	4.81	5.65
	Inf3	0.87	0	6.84	7.99
Liquid	-1.5	0.38	0	7.19	7.29
	0	0.48	0	5.69	5.87
	1	0.56	0	6.95	7.3
	2	0.52	0	5.92	6
	4	0.58	0	6.89	6.98
	6	0.66	0	6.94	7.02
	9	0.44	0	5.29	5.29
	12	0.43	0	5.37	5.37
	18	0.54	0	6.06	6.13
	23	0.47	0	7.46	7.54
Solid	-1.5	0.35	0	3.42	4.13
	0	0.59	0	3.28	4.4
	1	0.56	0	3.21	4.44
	2	0.52	0	2.77	3.64
	4	0.52	0	3.05	3.86
	6	0.5	0	3.08	3.84
	9	0.42	0	2.82	3.54
	12	0.45	0	2.94	3.49
	18	0.37	0	2.28	2.61
	23	0.41	0	2.88	3.42
	Eff	0.58	0	7.71	7.9

September 12, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	1.18	1.16	0.47	0.15	2.96
	Inf2	1.3	1.31	0.52	0.24	3.38
	Inf3	0.95	0.92	0.37	0.09	2.33
Liquid	-1.5	0.13	0	0	0	0.13
	0	0.15	0.09	0	0	0.25
	1	0.14	0.11	0	0	0.25
	2	0.11	0.08	0	0	0.18
	4	0.08	0	0	0	0.08
	6	0.14	0	0	0	0.14
	9	0.1	0	0	0	0.1
	12	0.14	0	0	0	0.14
	18	0.13	0	0	0	0.13
	23	0.12	0	0	0	0.12
Solid	-1.5	0.47	0.09	0	0.09	0.65
	0	0.68	0.38	0.13	0.12	1.32
	1	0.72	0.41	0.14	0.1	1.37
	2	0.59	0.33	0.12	0.11	1.15
	4	0.56	0.26	0.12	0.12	1.07
	6	0.52	0.21	0.1	0.13	0.96
	9	0.42	0.13	0	0.09	0.64
	12	0.47	0.11	0	0.13	0.7
	18	0.4	0.14	0	0.11	0.65
	23	0.47	0.1	0	0.11	0.68
	Eff	0.2	0	0	0	0.2

September 12, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	0.62	0.16	1.12	0.43	3.03
	Inf2	0.92	0.18	1.17	0.42	3.33
	Inf3	0.39	0.13	0.88	0.32	2.31
Liquid	-1.5	0.59	0.17	1.53	0.2	3.17
	0	0.42	0.14	1.38	0.28	2.54
	1	0.57	0.18	1.79	0.36	3.39
	2	0.47	0.18	1.67	0.33	3.07
	4	0.32	0.12	1.06	0.21	2.07
	6	0.74	0.19	1.78	0.27	3.61
	9	0.57	0.16	1.67	0.28	3.21
	12	0.8	0.2	1.92	0.3	4.02
	18	0.94	0.2	1.79	0.24	3.86
	23	0.79	0.18	1.57	0.16	3.44
Solid	-1.5	0.31	0.1	1.43	0	0.62
	0	0.62	0.08	1.25	0	0.66
	1	0.49	0.12	1.49	0	0.73
	2	0.23	0.11	1.02	0	0.53
	4	0.33	0.12	1.35	0	0.61
	6	0.53	0.09	1.35	0	0.63
	9	0.49	0.11	1.29	0	0.6
	12	0.57	0.11	1.25	0	0.71
	18	0.4	0.1	1.22	0	0.69
	23	0.64	0.08	1.58	0	0.68
	Eff	0.52	0.15	1.46	0.19	3.23

September 12, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	0.69	0	6.04	9
	Inf2	0.68	0	6.7	10.07
	Inf3	0.47	0	4.49	6.82
Liquid	-1.5	0.29	0	5.95	6.09
	0	0.41	0	5.17	5.41
	1	0.52	0	6.81	7.06
	2	0.44	0	6.16	6.34
	4	0.29	0	4.06	4.14
	6	0.49	0	7.08	7.22
	9	0.4	0	6.29	6.39
	12	0.45	0	7.69	7.83
	18	0.35	0	7.38	7.51
	23	0.24	0	6.38	6.5
Solid	-1.5	0.2	0	2.65	3.3
	0	0.23	0	2.84	4.17
	1	0.25	0	3.08	4.45
	2	0.18	0	2.06	3.21
	4	0.2	0	2.6	3.66
	6	0.21	0	2.81	3.77
	9	0.18	0	2.68	3.32
	12	0.22	0	2.85	3.55
	18	0.18	0	2.59	3.24
	23	0.17	0	3.16	3.84
	Eff	0.46	0	6.01	6.2

September 18, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	2.92	9.22	2.63	0.29	15.07
	Inf2	2.93	8.9	2.65	0.23	14.71
	Inf3	2.88	9.11	2.6	0.28	14.86
Liquid	-1.5	0.11	0	0	0	0.11
	0	0.35	1.01	0.15	0	1.5
	1	0.23	0.89	0.13	0	1.25
	2	0.21	0.87	0.12	0	1.21
	4	0.22	0.77	0.13	0	1.11
	6	0.21	0.73	0.14	0	1.08
	9	0.21	0.63	0.13	0	0.97
	12	0.19	0.41	0.09	0	0.69
	18	0.14	0.22	0	0	0.36
	23	0.13	0.2	0	0	0.33
Solid	-1.5	0.39	0.15	0	0.13	0.68
	0	0.95	1.88	0.53	0.14	3.5
	1	1.22	2.56	0.67	0.17	4.63
	2	1.26	2.52	0.66	0.2	4.64
	4	1.18	2.34	0.67	0.2	4.39
	6	1.14	1.98	0.59	0.2	3.92
	9	1.07	1.65	0.53	0.27	3.52
	12	0.85	1.21	0.39	0.15	2.59
	18	0.71	0.77	0.28	0.2	1.97
	23	0.67	0.53	0.23	0.23	1.67
	Eff	0.2	0.1	0	0	0.3

September 18, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	1.58	0.6	4.03	2.84	6.5
	Inf2	1.6	0.61	4.06	2.87	6.6
	Inf3	1.57	0.6	3.95	2.88	6.43
Liquid	-1.5	0.87	0.34	2.86	0.45	7.25
	0	1.12	0.42	3.33	1.11	6.68
	1	1.12	0.41	3.43	1.09	6.59
	2	1.08	0.4	3.29	1.22	6.42
	4	1.11	0.42	3.42	1.08	6.7
	6	1.02	0.36	3.21	1.01	6.29
	9	1.12	0.43	3.51	0.98	7.04
	12	1.02	0.37	3.18	0.52	6.84
	18	1.04	0.39	3.21	0.33	7.26
	23	1.07	0.4	3.42	0.76	7.14
Solid	-1.5	0.37	0.15	1.38	0	0.92
	0	0.28	0.11	0.99	0	0.8
	1	0.42	0.14	1.6	0.2	1.11
	2	0.41	0.16	1.51	0.21	0.97
	4	0.41	0.17	1.48	0	1.21
	6	0.4	0.15	1.42	0	1.18
	9	0.4	0.15	1.4	0	0.92
	12	0.42	0.15	1.48	0	0.94
	18	0.41	0.15	1.5	0	1.04
	23	0.44	0.17	1.55	0	0.94
	Eff	0.65	0.26	2.11	0.27	5.5

September 18, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	3.99	0.61	20.16	35.23
	Inf2	4.08	0.61	20.44	35.15
	Inf3	3.89	0.59	19.91	34.78
Liquid	-1.5	0.89	0	12.66	12.77
	0	1.81	0	14.48	15.98
	1	1.65	0	14.29	15.54
	2	1.73	0	14.15	15.36
	4	1.61	0	14.35	15.46
	6	1.59	0	13.48	14.56
	9	1.59	0	14.67	15.64
	12	0.98	0	12.91	13.61
	18	0.59	0	12.81	13.16
	23	1.24	0	14.02	14.35
Solid	-1.5	0.22	0	3.04	3.72
	0	0.2	0	2.39	5.89
	1	0.4	0	3.87	8.5
	2	0.44	0	3.7	8.35
	4	0.43	0	3.69	8.08
	6	0.39	0	3.55	7.47
	9	0.34	0	3.22	6.74
	12	0.24	0	3.24	5.82
	18	0.32	0	3.41	5.38
	23	0.28	0	3.37	5.04
	Eff	0.56	0	9.32	9.61

September 25, 1994

	Time	Palmitic	Linoleic	Oleic	Stearic	FA
	Inf1	10.05	25.99	9.84	1.17	47.06
	Inf2	10.77	27.76	10.55	1.25	50.32
	Inf3	11.75	30.28	11.49	1.3	54.83
Liquid	-1.5	0.1	0.09	0	0	0.18
	0	0.23	0.44	0.09	0	0.76
	1	0.19	0.43	0.09	0	0.71
	2	0.19	0.4	0.08	0	0.66
	4	0.17	0.36	0.08	0	0.61
	6	0.17	0.37	0.09	0	0.62
	9	0.16	0.24	0.06	0	0.46
	12	0.21	0.16	0.07	0	0.45
	18	0.14	0.11	0	0	0.25
	23	0.1	0	0	0	0.1
Solid	-1.5	0.49	0.17	0.06	0	0.72
	0	1.05	1.33	0.47	0.23	3.08
	1	1.04	1.44	0.48	0.14	3.11
	2	1.05	1.2	0.4	0.18	2.83
	4	0.88	1.04	0.37	0.16	2.46
	6	0.83	0.75	0.3	0	1.89
	9	0.74	0.85	0.52	0	2.11
	12	0.72	0.43	0.2	0.11	1.47
	18	0.59	0.21	0.12	0	0.91
	23	0.53	0.14	0.07	0	0.74
	Eff	0.35	0.14	0	0	0.48



September 25, 1994

	Time	Pimaric	Sandara	Isopimaric	Palus+LevDHA	
	Inf1	4.34	1.74	11.45	7.39	14.04
	Inf2	4.76	2.37	12.17	7.94	14.45
	Inf3	4.83	2.33	12.5	7.99	14.59
Liquid	-1.5	0.94	0.36	3.48	0.51	6.21
	0	1.02	0.36	3.49	0.88	5.67
	1	1.02	0.37	3.54	0.8	5.81
	2	1.01	0.35	3.51	0.84	5.8
	4	1.01	0.37	3.56	0.81	5.79
	6	1.01	0.37	3.57	0.73	5.87
	9	1.02	0.36	3.64	0.64	6.09
	12	1.04	0.38	3.74	0.58	6.32
	18	0.92	0.34	3.32	0.56	5.56
	23	0.96	0.35	3.47	0.26	6.31
Solid	-1.5	0.37	0.14	1.54	0	0.81
	0	0.45	0.17	1.85	0.18	0.98
	1	0.41	0.17	1.6	0.17	0.9
	2	0.39	0.13	1.59	0	0.81
	4	0.39	0.14	1.63	0.16	1.01
	6	0.39	0.14	1.53	0	0.87
	9	0.36	0.14	1.43	0	0.81
	12	0.37	0.13	1.48	0	0.77
	18	0.4	0.14	1.61	0	0.96
	23	0.4	0.13	1.65	0	0.84
	Eff	0.85	0.3	2.97	0.38	6.12

September 25, 1994

	Time	Abietic	Neoabietic	RA	RFA
	Inf1	11.15	2.37	52.49	99.54
	Inf2	11.45	2.37	55.5	105.82
	Inf3	12.44	2.69	57.37	112.19
Liquid	-1.5	0.83	0	12.32	12.51
	0	1.32	0	12.74	13.5
	1	1.24	0	12.78	13.49
	2	1.28	0	12.78	13.45
	4	1.23	0	12.77	13.39
	6	1.19	0	12.74	13.36
	9	0.99	0	12.74	13.2
	12	0.88	0	12.95	13.4
	18	1.34	0	12.04	12.29
	23	0.42	0	11.76	11.86
Solid	-1.5	0.23	0	2.09	3.8
	0	0.45	0	4.08	7.16
	1	0.4	0	3.65	6.76
	2	0.41	0	3.32	6.15
	4	0.4	0	3.74	6.19
	6	0.29	0	3.22	5.1
	9	0.25	0	2.98	5.09
	12	0.28	0	3.04	4.51
	18	0.26	0	3.37	4.29
	23	0.24	0	3.25	3.99
	Eff	0.74	0	11.36	11.84