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Use of Anareobic Baffled Reactors (ABR) Operated with and without Recycle for Treatment of Aircraft Deicing Fluid (ADF)

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USE OF ANAEROBIC BAFFLED REACTORS (ABR) OPERATED WITH AND WITHOUT RECYCLE FOR TREATMENT OF AIRCRAFT DEICING FLUID (ADF)

Michelle Barriault

A thesis submitted to the School of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master's of Applied Science in the Department of Chemical Engineering
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Abstract

Deicing fluid, which is used to prevent ice formation and to remove ice from aircraft, is used in large quantities in Canada every winter. It has been reported that the application of aircraft deicing fluid (ADF) to planes can result in as much as 96 % of the total glycol used being lost in the runoff. Since glycol has a very high chemical oxygen demand (COD), the resulting runoff will exert a high COD regardless of dilution. For this reason, it is desirable to treat the runoff before discharging it to a body of water.

Successful treatment of ADF has already been achieved using Upflow Anaerobic Sludge Blanket (UASB) reactors, yet the treatment has been limited by the maximum flowrate attainable before substantial washout of biomass occurs. The particular flow characteristics within Anaerobic Baffled Reactor (ABR) which lead to long solids retention times (SRT) have been found, in the current study, to overcome the SRT limitations and have resulted in biomass accumulation which would require biomass wastage to maintain constant biomass concentration within ABR operated without recycle or with a 6:1 recycle ratio.

A 1 % v/v ADF feed solution was successfully treated in ABR operated both with and without recycle at organic loading rates (OLR) varying between 4 and 11 g $COD/L_{reactor}{\cdot}d$. The ABR operated without recycle achieved a minimum hydraulic retention time (HRT) of 27 h with an acceptable COD removal efficiency of 89 % at an OLR of 6.2 g $COD/L_{reactor}{\cdot}d$, a specific organic loading rate (SOLR) of 0.30 g COD/g VSS·d and a specific substrate utilization rate (U) of 0.25 g COD_{rem}/g VSS·d. The ABR operated with a 6:1 recycle ratio achieved a better minimum HRT of 17 h with an acceptable COD removal efficiency of 93 % at an OLR of 9.9 g $COD/L_{reactor}{\cdot}d$, a SOLR of 0.35 g COD/g VSS·d and a U of 0.32 g COD_{rem}/g VSS·d. The SOLR were not found to vary significantly through most of the experimental period despite OLR increases due to biomass growth. It was also found that ABR treating ADF may be shut down for a period of three months and then restarted with ease. Recycle was found to reduce substrate toxicity effects through dilution and improved mixing and mass transfer through the ABR, thereby improving the U and allowing for greater throughput.

A mixing study has shown that ABR may be characterized as completely stirred tank reactors (CSTR) in series with low dead space and that the number of CSTRs could,

for the purposes of modeling, correspond to the number of actual compartments. However a CSTR-in-series model which was presented by Xing et al. (1991) was found to yield first order reaction rate coefficients which were correlated with substrate concentration driving force since the assumption made by Xing et al. (1991), that COD measurements can be considered representative of the acetic acid concentration does not hold and furthermore, since acetic acid is both created and consumed in anaerobic digestion and since high acetic acid concentration simultaneously inhibits and promotes methanogenesis, the assumption that the overall reaction rate is first order does not hold.

Résumé

Le fluide de dégivrage pour avion (ADF), qui est utilisé pour prévenir la formation de glace et pour enlever la glace des avions, et est utilisé en grande quantités au Canada à chaque hiver. L'application de ADF aux avions peut avoir comme résultat une perte te jusqu'à 96 % du glycol total utilisé. Puisque le glycol a une demande chimique en oxygène (DCO) très élevée, le ruissellement résultant exercera aussi un DCO élevé. Pour cette raison, il est préférable de traiter ce ruissellement avant de sa décharge.

Un traitement réussi de l'ADF a été accompli par des réacteurs de boues anaérobies avec débit ascendant (UASB), mais ce traitement était limité par le débit maximal possible avant qu'il y ait importante perte de biomasse. Les caractéristiques particulières de l'écoulement dans les réacteurs anaérobie à chicanes (ABR) qui permettent de longs temps de rétention de la biomasse (SRT) on permi, dans cette étude, de surmonter le limitation de SRT et on eu comme résultat une accumulation de biomasse qui nécessiterait un gaspillage de biomasse pour maintenir un niveau de biomasse continu dans les ABR fonctionnant sans recyclage ou avec un rapport de recyclage de 6:1.

Une solution de 1 % (v/v) de ADF à été traité avec succès dans des ABR fonctionnant avec ou sans recyclage à des taux de charge organique (OLR) variant entre 4 et 11 g DCO/$L_{réacteur}$·d. Le ABR fonctionnant sans recyclage a réussi un temps de rétention hydraulique (HRT) de 27 h avec une efficacité de traitement du DCO de 89 % et un OLR de 6.2 g DCO/$L_{réacteur}$·d, un taux de charge organique spécifique (SOLR) de 0.30 g DCO/g VSS·d et un taux spécifique d'utilisation de substrat (U) de 0.25 g $DCO_{enlevé}$/g VSS·d. Le ABR fonctionnant avec un rapport de recyclage de 6:1 a réussi un meilleur HRT minimum de 17 h avec une efficacité de traitement du DCO de 93 % à un OLR de 9.9 g DCO/$L_{réacteur}$·d, un SOLR de 0.35 g DCO/g VSS·d et un U de 0.32 g $DCO_{enlevé}$/g VSS·d. Les SOLR n'ont pas varié signifiquement durant la majorité de la période expérimentale malgré une augmentation du OLR à cause de la croissance de la biomasse. Il a été remarqué que les ABR traitant le ADF peuvent être éteints pour une période allant jusqu'à trios mois et peuvent être rallumés aisément. Il a été trouvé que le recyclage réduit l'effet de la toxicité du substrat par sa dilution et améliore le transfert de masse dans le ABR et en sorte améliore le U et permet une capacité de traitement améliorée.

Une étude de l'écoulement dans les ABR a démontré que ces réacteurs peuvent être caractérisés comme étant des réacteurs complètement mélangés (CSTR) en série avec très peu de zones mortes et que le nombre de CSTR en série pourrait être considéré comme étant égal au nombre de compartiments dans le ABR. Par contre il a été découvert que le modèle basé sur le principe de CSTR en série présenté par Xing et al. (1991) produit des coefficients de taux de réaction du premier ordre qui sont corrélés avec la concentration du substrat puisque l'hypothèses qu'une mesure du DCO peut être considérés représentative de la concentration en acide acétique et l'hypothèse que le taux global de réaction est du premier ordre ne tiennent pas car l'acide acétique est à la fois produite et consommée durant la digestion anaérobie et que des concentrations élevés d'acide acétique entravent et encouragent simultanément la méthanogénèse.

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To begin with I wish to thank Dr. Kevin Kennedy. Without his help, support and encouragement the document you hold in your hands would not exist. I would also like to thank my labmate Dr. Pham Thi Tham who was indispensable during times of frustration, casting light into some dark corners and providing helpful hints along the way. And let me not forget Francisco Aposaga without whom I would still be blundering about the lab looking for various parts and chemicals or cursing in frustration at broken down equipment.

I also wish to acknowledge the financial support provided by the National Science and Engineering Research Council, which kept me solvent and allowed me to eat something other than mac'n'cheese.

And of course, last but not least I have to thank my friends and family who encouraged me when I was frustrated, who distracted me when I was going crazy, and who always reminded me how to put things into perspective and laugh.

Et un merci à toi Maman, pour tout et rien en particulier.

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Nomenclature

AAFEB	anaerobic attached film expanded bed reactors
AAT	acetoclastic activity test
ABR	anaerobic baffled reactor
ADAF	aircraft deicing/anti-icing fluid
ADF	aircraft deicing fluid
AF	Anaerobic Filter
BOD	biochemical oxygen demand
BT	benzotriazole
COD	chemical oxygen demand
COD_{in}	chemical oxygen demand into the compartment
COD_{out}	chemical oxygen demand out of the compartment
COD_{rem}	chemical oxygen demand removed
CSTR	completely stirred tank reactor
CTMP	chemical thermal mechanical pulp
C_t	step input tracer concentration
D_f	molecular diffusivity
DiMeBT	dimethylbenzotriazole
F	dimensionless effluent concentration curve = C/C_{tracer}
HABR	hybrid anaerobic baffled reactor
HRT	hydraulic retention time
k	first order rate constant
k_{max}	maximum specific utilization rate of a given substrate
k^*	superficial first order reaction rate coefficient
log K_{OC}	coefficient of adsorption
K_s	half-velocity rate constant
M	mass
MeBT	methybenzotriazole
N	number of theoretical CSTR-in-series
n	number of compartment in ABR
NP	nonylphenol
OLR	organic loading rate
Q	influent substrate flowrate
R	recycle ratio
RSS_{cfm}	residual sum of squares corrected for the mean
RTD	residence time distribution
RWT	Rhodamine W.T. tracer
S	substrate concentration
SOLR	specific organic loading rate
SRT	solids retention time
t	time
TSS	total suspended solids
TSS_{cfm}	total sum of squares corrected for the mean
U	specific substrate utilization rate

UASB	upflow anaerobic sludge blanket reactor
V	volume
VFA	volatile fatty acids
VSS	volatile suspended solids
υ_{50}	the velocity at which 50 % of the biomass has washed out
W	mass of biomass
X	biomass concentration
$\bar{y}$	average value of y
$\hat{y}$	value predicted by the model
y_i	value of y obtained experimentally
θ	dimensionless time = t/HRT

Subscripts:

b	biomass
s	substrate
n	final compartment number
t	time
0	influent

other numerical subscripts indicate compartment numbers

Chapter 1

Introduction

Deicing fluid, which is used to prevent ice formation and to remove ice from aircraft, is used in large quantities in Canada every winter. It has been reported that the application of aircraft deicing fluid (ADF) to planes can result in as much as 96 % of the total glycol used being lost in the runoff. Since glycol has a very high chemical oxygen demand (COD), the resulting runoff will exert a high COD regardless of dilution. For this reason, it is desirable to treat the runoff before discharging it to a body of water.

Successful treatment of ADF has already been achieved using Upflow Anaerobic Sludge Blanket (UASB) reactors, yet the treatment has been limited by the maximum flowrate attainable before washout of biomass occurs. The particular flow characteristics within Anaerobic Baffled Reactor (ABR) which lead to long solids retention times (SRT) may overcome the inherent difficulties associated with the anaerobic treatment of ADF in UASB reactors. The ABR is a reactor design that uses a series of baffles to force the wastewater to flow over and then under them as it travels through the reactor from inlet to outlet. This creates conditions approaching plug flow. Bacteria within the reactor may rise then settle within the reactor due to gas production and flow characteristics, yet their movement through the reactor occurs at a very slow rate thus producing long SRT. Furthermore, the compartmentalisation of the bacteria may provide the ability to separate acidogenesis and methanogenesis longitudinally down the reactor, allowing the different bacterial groups to operate at their preferred conditions (i.e.: pH) (Barber and Stuckey, 1999).

The following research focused on the application of ABR for treatment of ADF. The effect of recycle on treatment efficiency was studied, and a CSTR-in-series based model which had been originally evaluated by Xing et al. (1991) for the treatment of molasses waste in a Hybrid Anaerobic Baffled Reactor (HABR) was evaluated for the treatment of ADF in ABR both with and without recycle.

Chapter 2

Literature Review

2.1 Aircraft Deicing Fluid:

Deicing fluid, which is used to prevent ice formation and to remove ice from aircraft, is used in large quantities in Canada every winter. In 1999, Betts reported that a medium sized airport might use over 1000 m^3 of fluid in one winter season and that 75-80 % of ADF applied to an aircraft ends up on the pavement in the deicing area, and that a further 15-20 % is sloughed off during taxiing and take-off. The discharge of ADF into the environment entrains two major concerns: (a) dissolved oxygen, (b) toxicity (Switzenbaum et al. 2001).

2.1.1 Dissolved Oxygen Considerations:

Since glycols are readily degradable by naturally occurring microorganisms, there is little concern about their persistence in the environment or of their bioaccumulation. Complete degradation has been shown to occur within 3-20 d depending on test conditions. (Miller,1979) Therefore, the concern lies in the oxygen consumed by the microorganisms during the biodegradation. Reported values of the biochemical oxygen demand (BOD) of pure propylene glycol approach 1,000,000 mg/L, while that of pure ethylene glycol has been reported to be in the range of 400,000-800,000 mg/L. (Switzenbaum et al., 2001) The BOD of different deicing fluids varies depending on the manufacturer, but Mulligan et al. (1997) report that Union Carbide UCAR XL 54 ADF exerts a BOD of 523,000 mg/L. In our laboratory testing, UCAR XL 54 ADF has been found to exert a COD of 700,000—800,000 mg/L. Due to its high BOD and COD values, ADF is of particular concern in surface and ground water environments. Ethylene and propylene glycols have been reported to have very low coefficients of adsorption onto organic carbon from water (log K_{OC} in the range of –2.14 to –0.52) and as such they are not readily retained by soil which speeds to leaching of the glycols into ground waters. And, since these glycols have very low vapour pressures (<0.2 mm Hg) they are not readily volitalized from an aqueous environment, and in consequence bacterial

activity and photo-oxidation are the major causes of glycol reduction in contaminated waters (MacDonald et al., 1993). Since aerobic biodegradation is the most important process affecting these glycols in surface water, the high BOD of ADF can deplete the dissolved oxygen content of the water resulting in eutrophication.

2.1.2 Toxicity Considerations:

The toxicity of certain ADF additives is also of concern. ADF contain whetting agents, corrosion inhibitors and pH modifiers (Holmgren and Forsling, 1995; Pham, 2002) although the exact formulation of these fluids is not known due to their proprietary nature. In general, fatty alcohols such as nonylphenol ethoxylates are employed as non-ionic surfactants. Corrosion inhibitors may include phosphates, silicates and amines. Inorganic bases such as KOH and NaOH are often used as pH modifiers (Holmgren and Forsling, 1995) and silver chelating agents such as benzotriazole may be added to reduce the hazards of ethylene glycol decomposition to a flammable ethylene oxide on silver-covered electrodes (Downes, 1968). These additives may be responsible for higher toxicity of ADF over that of pure ethylene or propylene glycol solutions to fish and insects. (Jank et al., 1973; Hartwell et al. 1993; MacDonald et al., 1993; Pillard et al., 2001). However, this toxicity is beyond the scope of this current study which will focus on the problem of dissolved oxygen reduction.

Aircraft deicing/anti-icing fluids (ADAF) are generally either propylene or ethylene glycol based. Due to a shortage of ethylene glycol in the winter of 1994, the United States began using predominantly propylene glycol based ADAF and since these fluids were found to be less toxic than their ethylene glycol counterparts, propylene glycol-based deicers are the only ADAF approved for purchase by the United States Air Force (McCarty and Willis, 1996). However, ethylene glycol-based deicers are still predominantly used in Canada (Simpson, 1997; Novak et al., 2000), and because of this, the ethylene glycol based UCAR XL 54 ADF was the ADAF used in this present study.

2.1.3 Types of Treatment:

Several types of treatment are currently available for ADF laden wastewaters from airport runways: aerobic treatment, anaerobic treatment, and recovery (Switzenbaum et al., 2001).

2.1.3.1 Aerobic Treatment:

Aerobic treatment is widespread. Most municipal wastewater treatment and many industrial treatment systems use aerobic treatment. Although effective in the degradation of many different wastes, aerobic treatment systems generally require a large energy input for aeration and mixing and produce large amounts of sludge which must be separated and processed before disposal. Many studies have shown that ethylene glycol and propylene glycol are degradable under aerobic conditions (Fincher and Payne, 1962; Kaplan et al., 1982; McGahey and Bouwer, 1992). Although some studies have achieved successful treatment of ADF using aerobic systems (Safferman et al. 1998; Nitschke et al., 1996), others have reported operational problems at publicly owned treatment works attributed to the high BOD concentration of ADF-laden waste streams (Jank et al., 1974).

2.1.3.2 Anaerobic Treatment:

Anaerobic treatment on the other hand, has several advantages over aerobic treatment. It does not suffer from aeration limitations, which reduces the energy requirement of anaerobic systems. Further, anaerobic systems are capable of removing the BOD from solution in the form of methane gas instead of just converting it from a dissolved waste to a solid waste in suspension. As the growth rate of anaerobic bacteria is considerably less than that of aerobic bacteria, less sludge is created, and fewer nutrients (i.e. N, P) are required. Moreover, anaerobic systems produce methane, which, although it is a greenhouse gas, can be burned to produce energy. Additionally, Jewell (1987) noticed that anaerobic biomass could remain dormant for long periods of time without significant loss of activity. This is due to a drastic reduction in the endogenous decay rate of anaerobic bacteria in starvation conditions (Speece,1996). Since ADF waste production is seasonal in nature, this particular trait is useful in that anaerobic systems could be shut down for the summer months and quickly restarted in the fall.

2.1.3.3 Recovery:

Glycols may be recovered from airport runoff using a system of nanofiltration to remove the high molecular weight additives and distillation to increase the concentration of glycol in solution (Switzenbaum et al., 2001). Reverse osmosis may also be used to concentrate dilute streams for subsequent recovery, however, waste solutions must be at least 10 % (v/v) glycol in order for this recovery to be feasible (USEPA, 1995). Glycol recovery has also only been found to be feasible at the largest airports (USEPA, 1994). Because of the oxygen limitations of aerobic treatment as well as the severe concentration limitations of glycol recovery, it appears that anaerobic digestion presents the best alternative for treatment of ADF laden wastewaters (Switzenbaum et al., 2001).

2.2 Review of Anaerobic Digestion:

Anaerobic digestion is the biodegradation of organic materials in the absence of oxygen into carbon dioxide and methane. This is a complex process that involves many different classes of bacteria and several intermediate steps which are represented schematically in Figure 2.1.

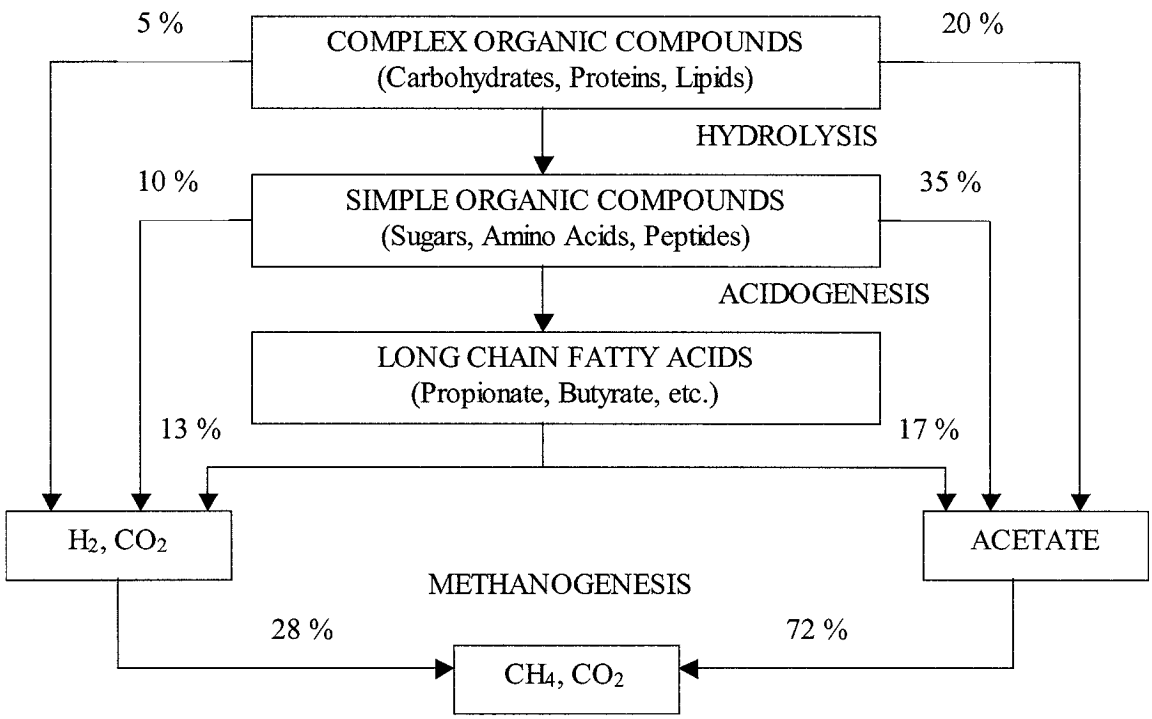

Figure 2.1: Anaerobic degradation pathways

If the substrate is a complex organic material, it must first be hydrolysed to simple organic compounds before it can be fermented to volatile fatty acids (VFA) by the acidogenic bacteria (acid formers). In the case of simple organic compounds, such as ethylene glycol, hydrolysis is not necessary. The longer chained fatty acids (i.e. acids with more than one carbon) are then converted to acetic acid and hydrogen gas by obligate hydrogen producing acetogens. Finally, the acetic acid and hydrogen gas can be converted to methane by methanogenic bacteria (methanogens) (Speece, 1996). There are two main types of methanogens: acetoclastic methanogens, which account for approximately 75 % of all methanogens, produce methane from acetic acid (Eqn. A) and hydrogen-ulilizing methanogens produce methane from hydrogen and carbon dioxide (Eqn. B). Approximately 25 % of the end products are produce through this route (Metcalf and Eddy, 1991).

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad \text{Eqn. A}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{Eqn. B}$$

This complex series of operations is rate controlled by the various anaerobic bacterial groups with the slowest growth rates and therefore the slowest metabolism rates, namely the acetic and propionic acid utilizing methanogens. This may cause an accumulation of these acids within the system with its concurrent reduction in bicarbonate alkalinity. This can lead to a drop in pH which can destabilize the microbial consortium. Further, this pH drop would tend to adversely affect the acetic and propionic acid utilizers disproportionately to the other groups, compounding the problem, which would further lower the pH. This phenomenon is known as reactor souring. Reactor souring can be avoided through careful monitoring of reactor pH and VFA levels or by buffering of the feed with bicarbonate alkalinity. At the first sign of increased VFA levels and/or pH levels, the feed to the reactor can be decreased or stopped and the reactor set to recycle only, thus allowing the bacterial consortia to consume the excess VFA without having the simultaneous production of VFA from incoming substrate.

Two main classes of bacteria are responsible for the production of methane from acetic acid: *Methanosaeta* (previously known as *Methanothrix*) as well as

Methanosarcina. These two groups differ in their substrate affinity (K_s) and their maximum specific utilization rate of this substrate (k_{max}). *Methanosaeta* are short rod shaped bacteria with a high affinity for acetic acid (acetate), (K_s = 20 mg/L) but have a relatively low maximum specific utilization rate, k_{max} = 2 to 4 g COD/gVSS·d (where VSS are volatile suspended solids). In contrast, *Methanosarcina*, which grow in clumps of four or more spherical bacteria, have a much lower substrate affinity, (K_s = 400 mg/L) but a higher maximum specific utilization rate, k_{max} = 6 to 10 g COD/gVSS·d. (Speece, 1996). Based on this, *Methanosaeta* is expected to predominate at low acetic acid levels (below 70 mg/L) whereas *Methanosarcina* would predominate at higher acetic acid concentrations. Photomicrographs of biomass in anaerobic reactors have confirmed this (Speece, 1996, Barber and Stuckey, 1999). However, it has been discovered that in the case of reactors where specific trace metals, such as iron, nickel or cobalt are not sufficiently bioavailable, *Methanosaeta* will continue to dominate even if the acetic acid concentration is over 1000 mg/L.

2.3 Anaerobic Treatment of ADF:

There have been several studies of high rate systems (systems where the biomass retention is not a direct function of HRT), as well as full scale treatment of ADF using anaerobic digestion. The Albany International Airport (Albany, NY), achieved high removal efficiencies for propylene glycol based ADF using a 700 L anaerobic fluidized bed reactor (AFBR) (Switzenbaum et al., 1999). At an organic loading rate (OLR) of 15 kg COD/m^3·d and influent COD of 5000 mg/L, COD removals efficiencies greater than 95 % were achieved. When operating at 25 kg COD/m^3d and HRT of 5 h, an average removal of 82 % was achieved. These high efficiencies achieved at full scale operation are indicative of the utility of ADF treatment in airport conditions.

Mulligan et al. (1997) successfully treated ethylene glycol based Union Carbide UCAR XL 54 ADF (the ADF to be used in this present study) using pilot plant scale anaerobic multiplate reactors operating at 39°C and 12 h HRT. Mulligan et al. report that at an OLR of 16.5 kg COD/$m^3_{reactor}$·d (13 kg BOD/$m^3_{reactor}$·d) and an influent COD of 8,500 mg/L 90 % COD reduction was achieved. This 900 L reactor contained 18.7 kg of biomass as total suspended solids (TSS), and as such, this OLR corresponds to a specific

organic loading rate (SOLR) of 0.79 kg COD/ kg TSS·d (0.63 kg BOD/kg TSS·d). Mulligan et al. (1997) did not report any problems with sludge deterioration or scum formation that were encountered when treating ADF using the activated sludge method.

In 1998, Darlington and Kennedy studied the mesophilic treatment of UCAR XL 54 ADF in Upflow Anaerobic Sludge Blanket (UASB) reactors for medium and high strength (5-20 g COD/L) wastes at OLR up to 38.7 kg COD/m^3·d. They achieved COD removal efficiencies between 70-98 %, thus demonstrating the feasibility of treatment of both high and medium strength ethylene glycol based ADF wastewaters using UASB reactors.

In the most comprehensive research of ADF treatment using UASB reactors to date, Pham (2002) noticed ADF toxicity effects to the granular biomass used in the study for reactors fed 1.6 % ADF by volume at medium organic loading rates (SOLR above 0.5 g COD/g VSS·d.) In contrast, good reactor stability and COD removal rates greater than 95 % at 1.2 % ADF by volume for reactor loadings approaching 0.73 g COD/g VSS·d were achieved. However, at 1.2 % ADF by volume, the biomass showed signs of stress in long term treatment. However, at 1 % ADF by volume, the biomass showed no signs of stress through the run time. For this reason, this present study intends to use a 1 % by volume ADF feed solution.

Pham (2002) further investigated the fate of ADF additives. Pham noted minimal sorption of benzotriazole (BT), 5-methyl-1 H-benzotriazole (MeBT), and 5,6-dimethyl-1 H-benzotriazole (DiMeBT) to aerobic granules. Greater sorption capacity of nonylphenol (NP) was noticed. Ethylene glycol degradation experiments showed that BT, MeBT, DiMeBT, and the non-ionic surfactant Tergitol NP-4 had no significant effects on acidogenesis and methanogenesis, but that significant inhibition of acetoclastic activity was observed for NP at 100 mg/L (38 % of that of controls), however both batch and continuous studies indicated that anaerobic degradation of NP occurs so the accumulation of NP within a recycling system should not be a concern.

In this study, Pham (2002) also reported that the substrate utilization rate was independent of the reactor biomass concentration. The maximum rate of substrate utilization and half-velocity constants for ADF treatment were found to be 28.4 g COD/L·d and 648 mg COD/L respectively. Also, for the treatment of 1.2 % ADF, the

biomass yield and endogenous decay coefficients were reported to be 0.027 g VSS/g COD and 0.012 d^{-1} respectively.

Although the treatment of ADF by UASB reactors proved to be successful, the maximum rate of treatment was found to be limited by biomass retention. In normal operation, at lower OLR, the biomass granules would rise within the UASB due to biogas bubbles which would attach to the granules. However, these bubbles would detach as the granule reached the liquid interface and the granules would fall back down to the biomass bed. At high OLR however, excess biogas production increased biomass loss as gas bubbles attached themselves to the anaerobic biomass granules and failed to detach before the granules were entrained into the effluent line. This limitation to the rate of treatment in UASB reactors, led to the application of ABR to ADF treatment.

2.4 Anaerobic Baffled Reactor Evolution:

Successful large-scale use of anaerobic treatment systems is dependent on the evolution of high rate systems, which retain biomass independently of the HRT. This feature reduces the reactor volumes required and allows for higher applied loading rates. There are many types of high rate systems in use worldwide such as: the UASB reactors, Anaerobic Filters (AF), and the Anaerobic Attached Film Expanded Bed reactors (AAFEB). AAFEB have reportedly achieved the greatest loading rate (120 kg COD/m^3.d) (Switzenbaum and Jewell ,1980), but are an inherently complex system with a high operating cost, which limit its practical use worldwide (Barber and Stuckey, 1999.) For this reason, this research proposes to study the application of Anaerobic Baffled Reactors (ABR) and the maximum loading rate applicable to them.

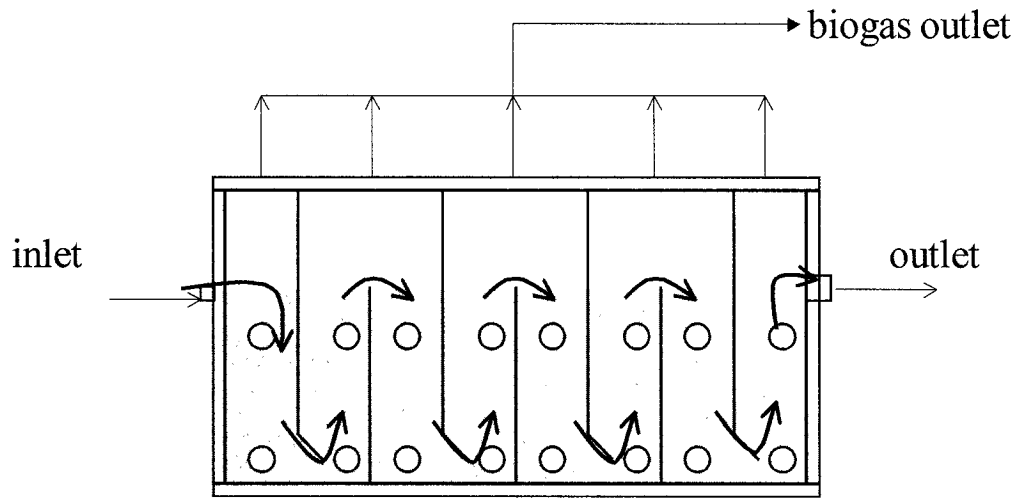

Figure 2.2: Schematic of an ABR

The Anaerobic Baffled Reactor (Figure 2.2) consists of a series of vertical baffles that force the wastewater to flow over and under them as it travels from the reactor inlet to the outlet. The lower baffles serve as a type of overflow weir dividing the reactor into compartments, each consisting of a downflow and an upflow section. The effluent of the first compartment is the influent for the second. This produces a plug flow or a reactor in series regime. This compartmentalisation may serve to separate acidogenic and methanogenic activities longitudinally through the reactor, allowing the reactor to behave as a naturally attenuated two-phase system without the associated control problems (Barber and Stuckey, 1999.) The baffles, especially when used in conjunction with granular anaerobic biomass, also serve to maintain long SRT regardless of HRT.

Although not commonly used on a large scale, the ABR has inherent advantages which Barber and Stuckey (1999) outlined briefly in tabular form and which are presented in Table 2.1.

Table 2.1: Advantages of ABR Use

Advantage
Construction
• Simple design
• No moving parts
• No mechanical mixing
• Inexpensive to construct
• High void volume
• Reduced clogging
• Reduced sludge bed expansion
• Low capital and operating costs
Biomass
• No requirement for biomass with unusual settling properties
• Low sludge generation
• High solids retention times
• Retention of biomass without fixed media or a solid-settling chamber
• No special gas or sludge separation required
Operation
• Low HRT
• Intermittent operation possible
• Extremely stable to hydraulic shock loads
• Protection from toxic materials in influent
• Long operation times without sludge wasting
• High stability to organic shocks

The main disadvantages that have been associated with ABR design are the shallow reactors that are required in order to maintain appropriate liquid and gas upflow velocities which require an increased footprint, and problems with maintaining even distribution of the influent and biosolids. These disadvantages however, are minor in comparison with the inherent advantages of ABRs.

The main factor behind ABR design changes has been to increase the SRT, but in some cases, modifications have been made to allow for treatment of recalcitrant and difficult to treat wastes or reduce capital costs. In 1981, Fannin and colleagues added baffles to a plug flow reactor treating high solids sea kelp slurry to maintain the slower growing methanogenic bacteria which where being pushed out by the accumulating solids. This had the added advantage of increasing substrate availability. In 1983, Bachmann et al. narrowed the downflow chambers to encourage cell retention in the

upflow chambers, and slanted the edges on the downward baffles to 40-45° to direct the flow towards the centre of the upflow compartment and thereby increasing mixing.

The first hybrid designs appeared next (Tilche and Yang, 1987). Modifications to the basic design were made to improve SRTs in order to treat high strength wastes. Tilche and Yang (1987) used a larger reactor which incorporated a solids settling chamber after the final compartment. Washed out solids were collected in the settling chamber and recycled to the first compartment. The authors also used packing at the liquid surface of each compartment to retain the bioflocs which became buoyant due to gas production. Because of lower washout, higher loading rates could be achieved. The authors also separated each gas chamber, thereby permitting the measurement of gas composition and production from each compartment. The separation of gas can enhance reactor stability by shielding syntrophic bacteria from the elevated levels of hydrogen which are found in the front compartments of the baffled reactor. None of these reactors however were used in conjunction with granular biomass. The reasoning behind this was to make startup costs lower however, the use of granular biomass within an ABR allows for operation at greater OLR due to the increased SRT (Grobicki and Stuckey, 1991).

Boopathy and Sievers (1991) further modified the baffled reactor in order to treat swine wastewater which had a high concentration of fine particulates. The main difficulties that they encountered in treating this waste was their inability to produce a floating sludge layer which would enhance the retention of the fine particulates within the reactor. In addition, the high flow velocities caused by the baffles further increased particulate entrainment and washout. For this reason, Boopathy and Sievers doubled the size of the first compartment dimensions in order to reduce upflow velocities.

2.5 Anaerobic Baffled Reactor Studies:

Boopathy and Tilche (1991) studied anaerobic digestion of high strength molasses wastewater in a hybrid anaerobic baffled reactor (HABR). This HABR design differs from the standard ABR design in that it contains packing in the upper portions of the upflow sections to reduce sludge washout. These researchers found that in their 3 compartment, 150 L reactor at an OLR of 12.3 kg COD/m^3·d (a SOLR of approx. 0.4 kg COD/kg VSS·d) a COD removal efficiency of 82 % could be achieved. Boopathy and

Tilche's study differed from previous studies in that they used a granular biomass. The granules appeared 30 days after start up and had an average diameter of 0.5 mm but grew through the run period. These dense granules differed from the previous bioflocs in that they had much better settling characteristics than the bioflocs and produced an effluent that was lower in suspended solids due to a decrease in biomass washout. The effluent was virtually free of VSS during low loading and reached a maximum of 17 g VSS/L at a loading of 30 kg COD/m^3·d.

For their part, Xing and Tilche (1992) studied the effect of HRT on HABR performance at constant loading. This study treated raw molasses wastewater in a HABR at an OLR of 10 kg COD/m^3·d in a similar reactor as that used by Boopathy and Tilche (1991). Xing and Tilche noted that at a HRT of 3.3 d, the VFA concentration was greater in the first compartment than in the other compartments or in the inlet. This was not unexpected as Henze and Harremoës (1983) pointed out, as an anaerobic digester operated at its maximum load would show an increased acid production and accumulation which would thereby inhibit the methanogenesis when there was a sudden increase in easily degradable organics. Xing and Tilche (1992) further noted that as the HRT increased (as feed rate was decreased) from 1 d to 6 d that removal efficiency dropped from 75 % to 40 %. It was postulated that as HRT increased, the substrate concentration driving force decreased and caused a decrease in COD removal efficiency.

Hutňan et al. (1999) presented a study on the methanogenic and nonmethanogenic activity of granulated biomass in a four compartment, 13 L ABR as compared to the activities in a 3.33 L UASB reactor in the treatment of starch and peptone wastewaters. These authors found that at an OLR of 10 kg/m^3·d the ABR showed a maximum specific hydrolytic activity of 36.8 kg COD/kg VSS·d, a maximum specific acidogenic activity of 38.1 kg COD/kg VSS·d and a maximum specific methanogenic activity of 1.51 kg COD/kg VSS·d while the UASB reactor had a maximum specific hydrolytic activity of 3.52 kg COD/kg VSS·d, a maximum specific acidogenic activity of 1.12 kg COD/kg VSS·d and a maximum specific methanogenic activity of 0.66 kg COD/kg VSS·d. These results further reinforced the fact that methanogenesis is the rate limiting step in anaerobic digestion but also demonstrated a strength of the ABR. Since the compartmentalization of the ABR allows the different bacterial groups to flourish in their

preferred conditions, the maximum specific activities in the ABR were found to be an order of magnitude greater than in the UASB reactor for hydrolytic and acidogenic activities and more than twice as great than that found in the UASB reactor in the critical, rate limiting, methanogenic activity.

Hutňan et al. (1999) observed that the specific hydrolytic and acidogenic activities were the highest in the first compartment while these activities remained almost constant in other compartments. The biomass in the first compartment was observed to be granular biomass of a light-grey colour with a large portion of suspended biomass while the biomass in the remaining compartments was fully granulated and black. The maximum specific methanogenic activity was obtained in the ABR's second compartment and it was assumed that the methanogenic activity in the first compartment was strongly influenced by the acidifying environment.

Nachaiyasit and Stuckey (1995) also noticed the de-linking of acidogenesis and methanogenesis in ABRs, with the number of acidogenic bacteria highest at the inlet and dropping towards the outlet of their 10 L, 8 compartment ABR which treated a 4 g COD/L sucrose/peptone wastewater. Like Xing and Tilche (1992) Nachaiyasit and Stuckey noted that as the HRT doubled from 40 h to 20 h, the increased substrate driving force led to an increase in activity and the COD removal efficiency remained constant at 98 %. These authors further noted that at start-up, granulation was observed in the first four compartments at loading rates of 0.13 kg COD/kg VSS·d which is lower than the loading rate found by Hickey et al. (1991) to be required for granulation in UASB reactors (0.3 to 0.5 kg COD/kg VSS·d).

These same authors further studied the effect of step changes in feed concentration as well as the effect of hydraulic shock loads (Nachaiyasit and Stuckey, 1997a; and Nachaiyasit and Stuckey, 1997b respectively.) They found the ABR to be extremely stable at constant HRTs to changes in feed COD and that the ABRs maintained high degrees of COD removal (>90 %) weeks after a large shock. The compartmentalized structure of the ABR was found to prevent much of the biomass from being exposed to low pHs during step shock organic loads and the reactors maintained the biomass in the reactor for long SRTs. Rapid fermentation of organic shock loads in the first compartment of the ABR was found to lower the pH and seemed to result in the

selection of a bacterial population that produced mainly acetic and butyric acids rather that propionic and formic acids which resulted in a more stable response to shock loads. COD removals of 98 % and 90 % were achieved at SOLR of 0.53 kg COD/kg VSS·d and 1.00 kg COD/kg VSS·d respectively.

In the case of hydraulic shock loads, Nachaiyasit and Stuckey (1997b) found the ABR to be stable to large transient shock loads (twentyfold decrease in the HRT for 3 h) and that although the biomass loss was substantial, it recovered to baseline performance in 9 h. The recovery time also appeared to decrease as the biomass concentration in the reactor increased. At a SOLR of 0.39 kg COD/kg VSS·d a specific substrate utilization rate (U) of 0.38 kg COD_{rem}/kg VSS·d was observed with an overall COD removal efficiency of 98 %. The greatest U (0.66 kg COD_{rem}/kg VSS·d) was observed at a SOLR of 0.73 kg COD/kg VSS·d and 90 % COD removal while the greatest SOLR (0.78 kg COD/kg VSS·d) resulted in a U of 0.41 kg COD_{rem}/kg VSS·d and an overall COD removal efficiency of 52 %.

Grobicki and Stuckey (1991) published what is perhaps the most comprehensive study of ABRs to date. Their publication presented a group of ABRs similar to those used in this present study but where the downflow section of each compartment was half the width of the upflow section while in the current study both widths are the same. (It should be noted that the 8 compartment reactor was subsequently used by Nachaiyasit and Stuckey in their studies, (1997a and 1997b)). Four reactors of three different volumes and with a varying number of compartments and containing a varying amount of granular biomass were used in the Grobicki and Stuckey study. The summary of the reactor configurations can be seen in Table 2.2 below.

Table 2.2: Characteristics of the reactors used in Grobicki and Stuckey (1990)

Reactor number	1	2	3	4
Working volume (L)	8.2	7.8	10.4	10.4
Number of compartments	4	6	8	8
Biomass inoculum (L/compartment)	1	0.67	1	0.5

These reactors were run without recycle with a feed concentration of 4,000 mg COD/L. Reactors 1 and 2 were fed a complex organic mixture while reactors 3 and 4 were fed a readily degradable sucrose mixture. Since the ethylene glycol feed used in

this current study is readily degradable, reactors 3 and 4 are of particular interest. Each of these two reactors were subjected to a series of hydraulic retention times varying from 20 h to 5 h, and finally to a shock load of 1 h.

Grobicki and Stuckey (1991) found that the major factor limiting overall reaction rate was the rate of mass transfer through the biomass aggregate. They found that although an increase in loading means an increase in the substrate concentration driving force, that above a SOLR of 1.5 g COD/g VSS·d the increase in the mass transfer rate is too slow to allow the reaction rate to rise enough to maintain high efficiency. The authors also postulated that an increase in average diameter of the granular biomass as the flowrate increases, since the smaller granules are washed out, may also lead to a decrease in efficiency. The authors determined that the optimum biomass concentration for reactors 3 and 4 at an OLR of 20 g COD/L·d was of 7 g VSS/$L_{reactor}$. The authors further noted that although within the ABR the HRT and SRT are strongly correlated, they had a non-linear relationship because shear stresses played a greater role at low HRT by breaking up granules and thereby increasing the washout of biomass.

In this study, COD removal at 20 h HRT was routinely over 95 % in all reactors with low washout of biomass. Very high specific reaction rates (as high as 1.1 g COD_{rem}/g VSS·d) were achievable at low biomass concentrations (3.5 g VSS/$L_{reactor}$) and high loading rates (SOLR of 1.4 g COD/g VSS·d) but these entailed a loss in overall reactor efficiency.

Grobicki and Stuckey also noted that there was an additional loss of biomass in one run because of a buildup of liquid inside the reactor, caused by a blockage in the effluent line.

In their 1992 publication, Grobicki and Stuckey presented a study of the hydrodynamic characteristics of the same four ABR configurations used in their 1991 publication. Using both clean and working reactors, the authors injected a one-shot input of tracer into the reactors. Fluorescein was used as the tracer for the clean reactors, while lithium chloride was used for the working reactors since lithium has been shown (Tomlinson and Chambers, 1979) not to absorb onto granular biomass and is not a nutrient for anaerobic granules. Reactors 1 and 2 were run clean (i.e. containing only water prior to injection of tracer) at HRT between 12 and 1h. The hydrodynamics of

these two reactors were then tested under working conditions (i.e. while the reactors, containing 6 g VSS/$L_{reactor}$, were treating the complex waste) at hydraulic retention time varying between 80 and 20 h. The hydrodynamics of reactors 3 and 4 under working conditions with two different biomass concentrations were also studied at HRT between 20 h and 5 h.

The residence time distribution (RTD) studies in the reactors without biomass revealed that reactor 2 (6 compartments) behaved as 6.4 theoretical Completely Stirred Tank Reactors-in-series (CSTR-in-series), while reactor 3 (8 compartments) behaved as 7.1 theoretical CSTR-in-series with very little dead space (between 1 % and 8 %.) The RTD studies for the working reactors showed a greater amount of dead space. In reactors 1 and 2, the dead space varied from 7 to 20 % with an average of 14 % for reactor 1 and 19 % for reactor 2. This is a significant increase from the 5 % dead space found in reactor 2 during the runs without biomass. However, since the tests with biomass were run at longer HRTs, the increase in dead space could be due either to the presence of biomass, or to the long residence times. For reactor 1 (4 compartments) the number of theoretical CSTR-in-series (N) was found to be 5.6 at 20 h HRT and reactor 2 (6 compartments) was found to have N = 6 at 20 h HRT.

The runs in reactors 3 and 4, where the amount of biomass varied, proved to be even more interesting. The dead space in reactor 3 was found to be 14 % with a trend towards decreasing dead space with decreasing HRT. The values for dead space calculated at 5 h HRT were low in both reactors and were of the same order as those in the runs without biomass which would indicate that at low HRT, the presence of biomass does not significantly increase the volume of dead space in the ABRs. Also, in both ABRs, N was close to the actual number of compartments. The authors also noted that at an HRT of 10 h channelling appeared to be significant, but that at an HRT of 5 h the increase in gas production as well as the increase in flowrate prevented channelling from occurring by maintaining the granular biomass beds in a fluidized state and thus decreasing the dead space.

Overall, the authors concluded that the more baffles a reactor contains, the less back mixing will occur, but that each individual compartment will be well-mixed. They further mentioned that the ABR may be characterized as CSTR-in-series with low dead

space and that the number of CSTRs could, for the purposes of modeling, correspond to the number of actual compartments. They pointed out that this characterization is more accurate at short HRTs (below 20 h) than at higher HRT due to increased gas production which improves mixing within each individual compartment at short HRTs.

2.6 Effect of Recycle on ABR Performance:

In general, recycle tends to reduce ABR removal efficiency because it results in the system moving away from plug flow conditions and pushes the system towards completely mixed conditions, and as such the mass transfer driving force for substrate removal is reduced despite a small increase in the loading rate due to the recycling of some COD from the effluent.

Chynoweth et al. (1980) found that 20 percent recycle (1:5 recycle) of their effluent had a positive effect on methane yield (an increase of 30 percent). They also found that the addition of a recycle stream was alleviated the problems of low pH caused by high levels of volatile fatty acids at the front of the reactor, and discourage gelatinous bacterial growth at the reactor inlet for the treatment of complex protein carbohydrate wastewater (Bachmann et al. 1983). Recycle has also been found to benefit the reactor through dilution of toxicants and reduction of substrate inhibition in the influent (Bachmann et al., 1985; Grobicki and Stuckey, 1991). Grobicki and Stuckey (1991) further note that theoretically, recycle should have a negative effect on reactor hydrodynamics by causing increased mixing which encourages solids loss, and disrupts microstructures of bacteria living in symbiotic relationships (Henze and Harremoës, 1983) and enhancing the amount of dead space (Grobicki and Stuckey, 1992; Nachaiyasit, 1995). Nachaiyasit (1995) found that dead space doubled when the recycle ratio (R) was increased from zero to 2, and also reported a sudden loss of solids when the recycle ratio was doubled. However, these results occurred with non-granular biomass and it is unknown whether this would hold true with granular biomass.

In treatment conditions, the mixing caused by recycle has been found to cause a return to single phase digestion, therefore the benefits arising from the separation of the acidogenic and methanogenic phases of treatment within ABR would be partially lost

when recycle is used. Bachmann et al. 1985 saw that the methanogenic activity was more uniformly distributed through the reactor when recycle was used.

Barber and Stuckey (1999) point out that the overall benefits of recycle are unclear and that the ultimate use of recycle will depend on the type of waste being treated. If pH problems are severe, the influent has high levels of toxic material, or high loading rates are preferred, then recycle will be beneficial. They believe that recycle should be used with caution, and only when absolutely necessary. These authors summarize the advantages and disadvantages of recycle use as outlined in Table 2.3.

Table 2.3: Advantages and disadvantages of effluent recycle in ABR (Barber and Stuckey, 1999)

Advantages	Disadvantages
1.Front pH increased	1.Overall efficiency reduced
2. Reduction of influent toxicity and substrate inhibition	2. Increased solids loss
3. Higher loading rates possible	3.Increased hydraulic dead space
4. Better substrate biomass contact	4.Disruption of bacterial communities and bioflocs
	5. Encourages one-phase digestion

Since ADF waste has inherent toxicity (Pham, 2002) benefit of the dilution effect of the recycle may predominate over any possible negative effects due to increased mixing and as such, this current study proposes to examine the effect of recycle on ADF treatment by operating ABRs both with and without recycle.

2.7 Modeling of ABR Treatment:

In a quest to better understand ABR operation and to predict reactor performance, attempts have been made to develop a model for ABR reactors.

The consumption of substrate and the production of end-products and new biomass, whether aerobic or anaerobic, is difficult to model accurately due to the complex nature of bacterial growth and its relationship to substrate uptake. The simplest models are those which represent the reactor as a black-box CSTR-type reactor. The simplest of these uses first order kinetics, where the change in substrate concentration with time in the reactor is represented by:

$$\left(\frac{dS}{dt}\right) = -kS \,. \qquad \text{Eqn. 1}$$

where S is the substrate concentration (MV^{-1}) and k is the first order rate constant with units of t^{-1}. This equation however does not account for the increase in substrate consumption with an increase of biomass in the system. To account for this, equation 2 was developed which is a first order reaction with respect to substrate concentration and also first order with respect to biomass concentration.

$$\left(\frac{dS}{dt}\right) = -kSX \qquad \text{Eqn. 2}$$

Here, X represents the concentration of biomass in the reactor (M_bV^{-1}) and the units of the rate constant k become $V\ M_b^{-1}\ t^{-1}$. Although X should be the actual active biomass concentration, it is very difficult to measure. Often, the X term is approximated by the VSS concentration within the reactor. Due to its simplicity, and the ease in which the variables of this equation may be measured, this rate equation has become a staple in modeling of aerobic systems (Metcalf and Eddy, 1991) and Chynoweth and Isaacson (1987) suggest that this equation may be used reliably in anaerobic digestion as well. This equation has become the basis of an ABR model as well (Xing et al., 1991).

It should however be noted that equation 2 does not take into account the effect of substrate limitation on the rate of reaction. If the amount of substrate is below a certain threshold, the bacteria within the system must compete for the available resources. This leads to a decrease in the overall substrate utilization rate. Monod developed an empirical hyperbolic relationship known as the Monod equation (Eqn. 3) which has been shown to adequately describe the utilization of substrate in most continuous-growth culture systems in substrate-limited conditions. (Metcalf and Eddy, 1991; van Haandel and Lettinga, 1994). However, this model assumes that the growth of a pure culture on a single substrate is similar to that of mixed cultures on complex organic wastes (Chynoweth and Isaacson, 1987).

$$\left(\frac{dS}{dt}\right) = -\frac{kX_b S}{K_S + S} \qquad \text{Eqn. 3}$$

Here, the specific substrate utilization rate constant k and the half-velocity rate constant K_S, which has been defined as the substrate concentration at one-half the maximum growth rate (MV^{-1}) (Metcalf and Eddy, 1991), are generally determined using the Lineweaver-Burke equation (Eqn. 4)

$$-\left(\frac{X}{dS/dt}\right) = \frac{1}{U} = \frac{K_S}{k}\frac{1}{S} + \frac{1}{k} \qquad \text{Eqn. 4}$$

Here, U, the specific substrate utilization rate ($M_s\ M_b^{-1}\ t^{-1}$) represents the rate of consumption of substrate per unit of biomass. This in effect accounts for the increased rate of consumption with an increase in bacterial population, as does equation 2 earlier. In fact, with this nomenclature, equation 2 could be rewritten as:

$$\frac{dS/dt}{X} = U = -kS. \qquad \text{Eqn. 5}$$

Using the Lineweaver-Burke equation, k and K_S can be determined graphically knowing the substrate concentration, the amount of biomass in the reactor, and the substrate removal rate. However, due to its reliance on a linear graphical fit of reactor performance data, this method can prove difficult to use reliably.

Using basic kinetic reaction rate equations, several models have been developed to predict ABR performance. Four such models are summarised in Table 2.4.

Table 2.4: Model equations for ABR systems (Barber and Stuckey, 1999)

No.	Substrate model equations	Ref.
1	$\frac{dS}{dt} = -aCS^q + QS_0 - QS,\ S = S_0 - \left(\frac{a}{Q}\right)CS^q$	Bachmann et al., 1983
2	$D_f\left(\frac{\partial^2 S_f}{\partial z^2}\right) = \left(\frac{kS_f X_f}{K_s + S_f}\right)$	Bachmann et al., 1985
3a	$S_n = \frac{S_0}{(1 + k_1W_1/Q)(1 + k_2W_2/Q)...(1 + k_nW_n/Q)}$	Xing et al., 1991
3b	$S_n = \frac{S_0(1+R)^{n-1}}{(1 + R + k_1W_1/Q)(1 + R + k_2W_2/Q)(1 + R + k_3W_3/Q)...(1 + R + k_nW_n/Q) - (1+R)^{n-1}R}$	Xing et al., 1991
4	$D_f\left[\frac{\partial^2 S_f}{\partial r^2} + 2r\left(\frac{\partial S_f}{\partial r}\right)\right] = \left(\frac{kX_f S_f}{K_S + S_f}\right)$	Nachaiyasit, 1995

where: a = surface area per unit reactor volume (L^{-1}), C = variable-order reaction coefficient, D_f =molecular diffusivity in biofilm (L^2t^{-1}), k = maximum specific rate of substrate utilization (t^{-1}), K_S =half velocity constant ($M\ L^{-3}$), Q = specific flow rate ($V\ t^{-1}$), q = variable order reaction order, r = radius of a three-dimensional spherical particle (L), R = recycle ratio, S = substrate concentration (ML^{-3}), S_0 = influent concentration (ML^{-3}), S_f = substrate concentration in biofilm (ML^{-3}), S_n = effluent substrate concentration (ML^{-3}), W = mass of biomass (M), z = distance normal to biofilm surface (L), Numerical subsripts refer to compartment number.

In the first model presented in Table 2.4 Bachmann et al. (1983), who had found similar treatment behaviour under identical conditions in an ABR, anaerobic filter and a rotating biological disc reactor, represented the biomass particles found in the sludge bed of the ABR as fluidised spheres with a surface area through which the solute must diffuse for bacterial consumption. Therefore, they used a combination of a fixed film model (Williamson and McCarty, 1976) along with a variable order model (Rittmann and McCarty, 1978) which incorporated the concepts of liquid-layer mass transfer, Monod characteristics, and molecular diffusion to accurately describe the process. However, the application of this model required the estimation of the specific surface area of the biomass in each of the reactor compartments which proved difficult and the model did not give a realistic interpretation of their data as the assumption of constant diffusion layer depth was found to be unrealistic.

In further studies, Bachmann et al. (1985) ran ABR with a sucrose based influent with a substrate concentration of 8000 mg COD/L and achieved COD removals in the range of 55-93 % while operating between OLR of 36.2-2.5 g COD/L·d. In this study, the authors represented the reactor performance using Monod kinetics (equation 2 of

table 2.4), but the evaluation of the model required the use of kinetic constants such as k, Ks and D_f (molecular diffusivity in the biofilm) that were assumed to be similar to standard kinetic constants evaluated in previous anaerobic digestion studies. The assumption of kinetic constants makes this model difficult to apply reliably.

Nachaiyasit (1995) further improved the model put forth by Bachmann et al. (1985) by deriving a spherical model. Nachaiyasit postulated that at high loading rates, the film supports were not sufficiently flat to be considered as such, since the biofilm thickness would be greater than about 1 % of the radius of curvature in these conditions. She noted, that since the biomass particles within the reactor acted as fluidized spheres with a surface area through which the substrate must diffuse, a spherical model would be more appropriate. However, this model also relied on kinetic constant calculations. Since the accuracy of any model depends critically on the wastewater and substrate used, kinetic data would have to be experimentally determined for each compartment once the reactor is at steady state (Bachmann et al., 1985) by using anaerobic bioassays. This approach may have enabled Nachaiyasit's spherical model to give a more realistic fit at the front of the reactor than did Bachmann et al. (1985), however the reliance on such kinetic data makes the models evaluated by Bachmann et al. (1983 and 1985) as well as that evaluated by Nachaiyasit (1995) difficult to use. Speece (1996), noted that the bioassay bottle tests may not be held representative of reactor performance. In these bottle tests the substrate concentration drops as it is consumed therefore decreasing the substrate concentration driving force as the test progresses. However, in the functioning reactor the substrate concentration within any given compartment will remain constant at any given steady state condition. As such, all these mechanistic models rely on bottle tests of questionable significance. The model evaluated by Xing et al. (1991) (Table 2.4, equations 3a and 3b) on the other hand is generally an empirical model with limited mechanistic parameters. Further, this model need not rely on bottle tests, as the rate coefficients (k) can be calculated from operational data knowing the substrate concentrations in each of the reactor compartments. Since each of the parameters in the Xing et al. (1991) model are easily measurable, it was decided to test this model for the treatment of ADF waste in an ABR.

2.7.1 Model Evaluated by Xing et al. (1991):

The model presented by Xing et al. (1991) to represent the performance of an HABR is based upon the first order kinetics presented earlier (Eqn. 2) and on the assumption that each of the compartments within the HABR act as a CSTR, and that the HABR as a whole acts as CSTR-in-series. If each of the compartments within the HABR (or ABR) act as a CSTR (i.e. perfectly mixed), then it can be assumed that the substrate concentration would be the same at all points in the compartment, and that this concentration would be equal to the concentration at the effluent of this compartment. (Levenspiel, 1999) In an HABR, as in an ABR, the effluent of the first compartment will be the influent for the second compartment, and the effluent of the second compartment will be the influent for the third compartment and so on through the reactor. As the number of compartments in the HABR (ABR) increases, it would follow that the number of CSTR-in-series would increase. As the number of CSTR-in-series increases, the mixing regime will approach that of a plug flow reactor (PFR) (Levenspiel, 1999). Further, Levenspiel (1999) points out that in the case of CSTR-in-series with recycle and throughflow, where the recycle is relatively rapid compared to the throughflow, the system as a whole would act as one large CSTR. The model put forth by Xing et al. (1991) accounts for this effect and therefore, if without recycle the HABRs (ABRs) can be said to behave as CSTR-in-series wherein the number of theoretical CSTRs is equal to the number of compartments, then the model used by Xing et al. (1991) should also account for the hydraulic effects of the recycle.

As in the previous models, the Xing et al. (1991) model assumes that acetoclastic methane production as the rate-limiting step, and as such, the rate constant calculated is assumed to be the rate of acetoclastic methane production.

The Xing et al. (1991) model is based on the mass balance:

$$\frac{dS}{dt}V_1 = QS_0 + RQS_n - (1+R)QS_1 - k_1 S_1 X_1 V_1 \qquad \text{Eqn. 6}$$

where: S_0 inlet substrate concentration (g/L)
S_n substrate concentration out of the final compartment (g/L)
R recycle ratio
k specific substrate utilization rate coefficient (d^{-1})
V volume of the compartment
X is the concentration of biomass in the compartment (g VSS/L)

Q influent substrate flowrate (L/d),
and the subscripts represent the compartment to which the particular mass of biomass or specific substrate utilization rate coefficient applies.

At steady state (i.e dS/dt = 0) this mass balance (Eqn. 6) defines the substrate utilization rate (the final term on the right hand side (g/d)) as the difference between the influent substrate concentration to compartment 1 (first two terms on the right hand side) and the effluent substrate concentration out of compartment 1 (the third term on the right hand side).

Knowing that the concentration of granular biomass in each compartment is equal to the mass of biomass (W) in grams, divided by the volume of the compartment (V) in litres, that is; $X_1 = \frac{W_1}{V_1}$, Xing et al. (1991) substituted the mass of biomass into the mass balance and solved for a system of *n*-CSTR-in series (where n is the number of compartments in the HABR and the other parameters are as defined previously).

$$S_n = \frac{S_0(1+R)^{n-1}}{(1+R+k_1W_1/Q)(1+R+k_2W_2/Q)(1+R+k_3W_3/Q)...(1+R+k_nW_n/Q)-(1+R)^{n-1}R} \qquad \text{Eqn.7}$$

Xing et al. (1991) determined model parameters (k_1 through k_n) by the least square method based upon experimental data. This study assumed that the substrate concentration could be approximated by COD measurements, and that the mass of active biomass could be approximated by the VSS of the biomass.

2.7.1.1 Xing et al. (1991) Experimental Results:

In their study, Xing et al. (1991) used a modified HABR to treat a high strength molasses wastewater in mesophilic conditions. The Plexiglas reactor used in this study was comprised of 3 compartments and a final settler. The working volume of each of the 3 compartments was 50 L with a settler at 15 L. The first two compartments contained a 10 cm layer of plastic Pall rings (diameter 38mm, specific surface area 142 m^2/m^3 and a void space of 94 %.) situated just below the liquid surface and the final chamber had a modular corrugated block (Eco Trick® 200 m^2/m^3, 98.5 % void space) occupying it's upper half. The bioflocs entrained by the evolution of gas bubbles would strike the

packing and disengage from the gaseous bubble to settle back down to the base of the reactor. It should be noted however that this study did not utilize granular biomass and it has been shown that the use of highly settleable granular biomass renders packing unnecessary (Grobicki and Stuckey, 1991).

The HABR studied by Xing et al. (1991) was seeded with a combination of digested sewage sludge and cow manure sludge to 1/3 full and treated molasses wastewater. Following the start-up period, the reactor contained 4.1 g VSS/L. It should be noted, that unlike ADF wastewater, molasses wastewater is non-toxic and modeling results may differ in consequence. The HABR was operated at OLR varying between 0.97 kg COD/m^3·d and 28 kg COD/m^3·d and the COD in each compartment as well as the amount of biomass in the reactor were monitored for each of 4 steady-state conditions (OLR = 5.5 kg/m^3·d, 10.7 kg/m^3·d, 11.8 kg/m^3·d and 16 kg/m^3·d) .

2.7.1.2 Reactor Performance:

The soluble COD removal efficiency was found to decrease with increasing loading, from an initial removal efficiency of 90 % at an OLR of 8 kg COD/m^3·d up to the maximum load of 28 kg COD/m^3·d where the COD removal efficiency was of 50 %.

2.7.1.3 Model Evaluation and Predictions:

If the model created by Xing et al. (1991) is to be applied to an ABR with four compartments and granular biomass, as in the case of the proposed study of ADF treatment in ABRs, the overall form of the outlet concentration equation first presented in Table 2.4 becomes:

$$S_4 = \frac{S_0(1+R)^{4-1}}{(1+R+k_1W_1/Q)(1+R+k_2W_2/Q)(1+R+k_3W_3/Q)(1+R+k_4W_4/Q)-(1+R)^{4-1}R}, \qquad \text{Eqn. 8}$$

where:

S_0	inlet COD (g/L)
S_4	COD out of the fourth (and last) compartment (g/L)
R	recycle ratio
k	specific COD utilization rate coefficient (d^{-1})
W	mass of granular sludge in chamber (g VSS)
Q	influent substrate flowrate (L/d),

and the subscripts represent the compartment to which the particular mass of granular sludge or specific substrate utilization rate coefficient applies.

Without recycle, Eqn. 8 becomes:

$$S_4 = \frac{S_0}{(1 + k_1 W_1 / Q)(1 + k_2 W_2 / Q)(1 + k_3 W_3 / Q)(1 + k_4 W_4 / Q)}. \quad \text{Eqn. 9}$$

For S_1, the substrate concentration in the first compartment, the equation for a reactor with recycle would reduce to:

$$S_1 = \frac{S_0 + RS_4}{(1 + R + k_1 W_1 / Q)} \quad \text{Eqn. 10}$$

since in effect, one single compartment acts as a single CSTR-in-series (without recycle R = 0). From this and knowing the substrate concentration of the feed (S_0) as well as the substrate concentration at the outlet of compartment 1 (S_1), the recycle ratio R, and the mass of granular biomass in compartment 1 (W_1), parameter k_1 can be calculated. Then, k_2 could be calculated, using the measured value of S_1 and the
equation:

$$S_2 = \frac{S_1(1 + R)}{(1 + R + k_2 W_2 / Q)}. \quad \text{Eqn. 11}$$

Subsequently, using the measured values of S_2 and S_3 the coefficients for k_3 and k_4 can be calculated from

$$S_3 = \frac{S_2(1 + R)}{(1 + R + k_3 W_3 / Q)} \text{ and,} \quad \text{Eqn. 12}$$

$$S_4 = \frac{S_3(1 + R)}{(1 + R + k_4 W_4 / Q)} \text{ respectively.} \quad \text{Eqn. 13}$$

Having taken COD profiles at 4 organic loading rates (5.5 kg/m^3·d, 10.7 kg/m^3·d, 11.8 kg/m^3·d and 16 kg/m^3·d), Xing et al. (1991) used this method to calculate each of their k coefficients (Table 2.5) then took the average value of the k coefficient for each compartment thus creating $k_{1\ \text{average}}$, $k_{2\ \text{average}}$ and $k_{3\ \text{average}}$ which were then used in conjunction with equations 10 through 13 (where recycle = 0) to calculate predicted COD measurements for each compartment which were then compared with the measured COD values.

Table 2.5: Xing et al. (1991) model parameters

Parameter	Compartment 1	Compartment 2	Compartment 3
k_i (1/d)	0.023	0.019	0.029

When the experimental data and model simulation results were compared, they were found by Xing et al. (1991) to be acceptable for loading rates between 2 and 25 kg/m^{3}d. The authors then summarized their results with the following predictions:

1- for constant organic loading, the treatment efficiency would increase with increasing influent substrate concentration.
2- as HRT is reduced the efficiency of the reactor will decrease
3- performance deteriorated with increasing loading (11-16 kg COD/m^{3}d) with a constant sludge weight
4- an improvements in COD removal efficiency was observed with increasing sludge weight until a certain concentration was reached, above which reactor performance becomes independent of biomass concentration
5- an increase in recycle ratio would coincide with a subsequent decrease in COD removal.

The author further noted that in comparison with other process variations, such as influent substrate concentration and flow rate, the predicted effect of recycling ratio on treatment efficiency would be relatively small. According to the model evaluation, when the recycling ratio increased from 0 to 10, the corresponding treatment efficiency only decreased about 10 %. Nachaiyasit and Stuckey (1995) noted this effect, but linked it to the increased mixing due to recycle. Nachaiyasit and Stuckey postulated that the increased mixing would lead to a decrease in COD removal efficiency with increased recycle due to the destruction of biomass flocs associated with increased shear forces. They further note that the decreased substrate concentration driving force would also decrease the substrate removal efficiency for ABR operated with recycle. However, it is important to remember that Barber and Stuckey (1999) point out that the overall benefits of recycle are unclear and that the ultimate use of recycle will depend on the type of waste being treated. If pH problems are severe, the influent has high levels of toxic material, or high loading rates are preferred, then recycle will be beneficial. Nachaiyasit and Stuckey (1995) used a carbohydrate (sucrose) feed while Xing et al. (1991) used a

molasses wastewater. Both of these wastes are non-toxic, and as such the effect of recycle on the treatment efficiency of ADF wastes may differ.

2.7.1.4 Inconsistency in the Model Evaluated by Xing et al. (1991):

In attempting to reconcile the results predicted by Xing et al. (1991) with this author's study, it became apparent that there was an inconsistency in the model presented by Xing et al. (1991). Referring to equation 6 and examining the rate of substrate utilization term (final term on the right hand side) the problem becomes apparent. The units within the Xing et al. (1991) model are inconsistent. In order to maintain consistent units, k must have units of L/gVSS·d and not 1/d as claimed in Xing et al. (1991). Upon closer examination, the full units of k are found to be (g COD removed/g COD)/(g VSS/L)·d and are the correct units for a first order reaction rate coefficient where the rate is a function of the amount of biomass in the system (see equation 2). This implies that the "specific COD utilization rate coefficients" (k) calculated by Xing et al. (1991) would be a function of the amount of biomass within the reactor at any given time and since this value is not controllable due to biomass growth and biomass carryover, the predictive capabilities of this model may be limited.

This present thesis intends to present a mixing study to determine whether ABR reactors operated at HRT varying between 36 h and 1 h can be said to behave as CSTR-in-series since according to Barber and Stuckey (1999) the number of theoretical compartments determined by mixing studies should be used in CSTR-in-series models and not the actual number of compartments. Models such as that described by Xing et al. (1991) rely on the number of theoretical compartments being identical to the actual number of compartments. Thereafter, it is proposed to apply the Xing et al. (1991) model to an ABR with and without recycle to determine the extent to which the predictions made by Xing et al. (1991) hold true, regardless of the error in rate parameter.

Chapter 3
Materials and Methods

3.1 Apparatus, Start-up and ADF Treatment:

Two bench scale ABRs were operated in continuous mode. Each of these 300 × 600 × 250 mm (h × l × w) rectangular Plexiglas™ reactors were subdivided into four 7.7 L compartments by a vertical baffle rising 200 mm from the reactor bottom defining the liquid level height therein and thereby the working volume of the reactors. Each of these compartments were comprised of a down-flow section and an upflow section that were defined by a vertical baffle coming down from the top of the reactor and terminating with a 45° angled portion which was used to promote mixing within the upflow section of the compartment. Both reactors were inoculated with 10 L of anaerobic granular biomass obtained from Lake Utopia Paper, a chemical thermal mechanical pulp (CTMP) treatment plant located in St. George New Brunswick, Canada. The 10 L of biomass were separated evenly between each of the four compartments within each reactor (i.e. 2.5 L/compartment.) Although both reactors were equipped with an internal recycle line set at a 6:1 recycle ratio, only one reactor was operated with recycle, where the other was operated without. This second reactor was nonetheless equipped with a recycle line so that, should reactor upset occur, feed could be shut off and the reactor set to recycle only in order to decrease the VFA levels.

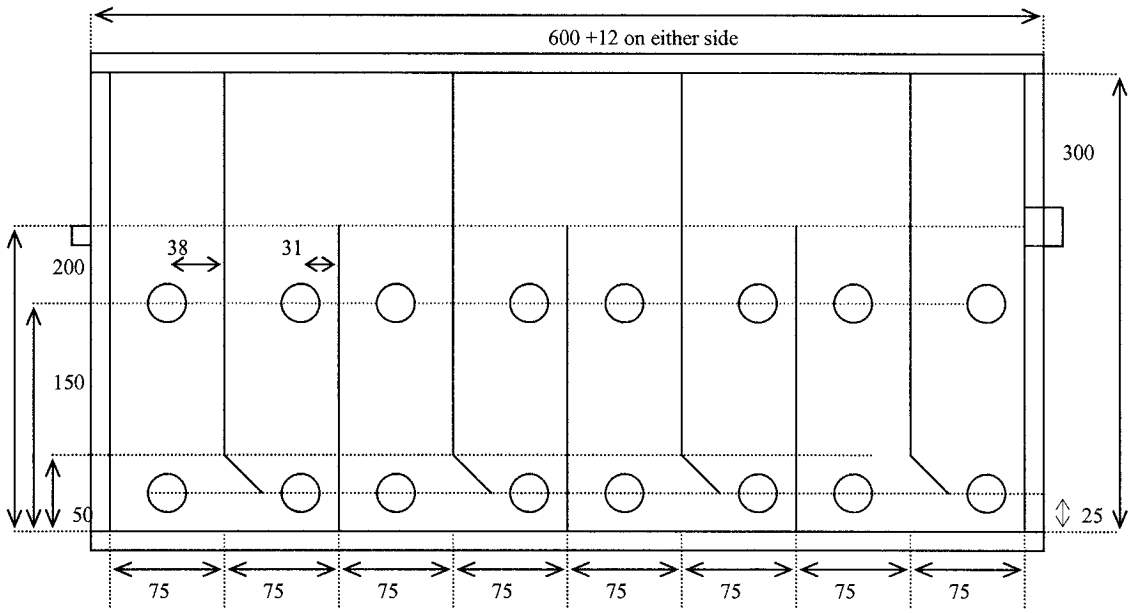

Figure 3.1: Anaerobic baffled reactor, all dimensions in mm

Referring to Figure 3.1, the inlet and outlet ports visible at either end of the ABR, were positioned so that the liquid level within the reactor was equal to the height of the rising baffle. As such, the rising baffle acted as a type of overflow weir, therefore promoting the retention of biomass. As shown in Figure 3.2, the feed for each of the ABRs was drawn from an insulated main feed recirculation line. This system allowed the feed to be maintained at 4°C until fed to the ABRs. The relatively small quantities of feed (with respect to volume of reactor contents) prevented any significant temperature shock.

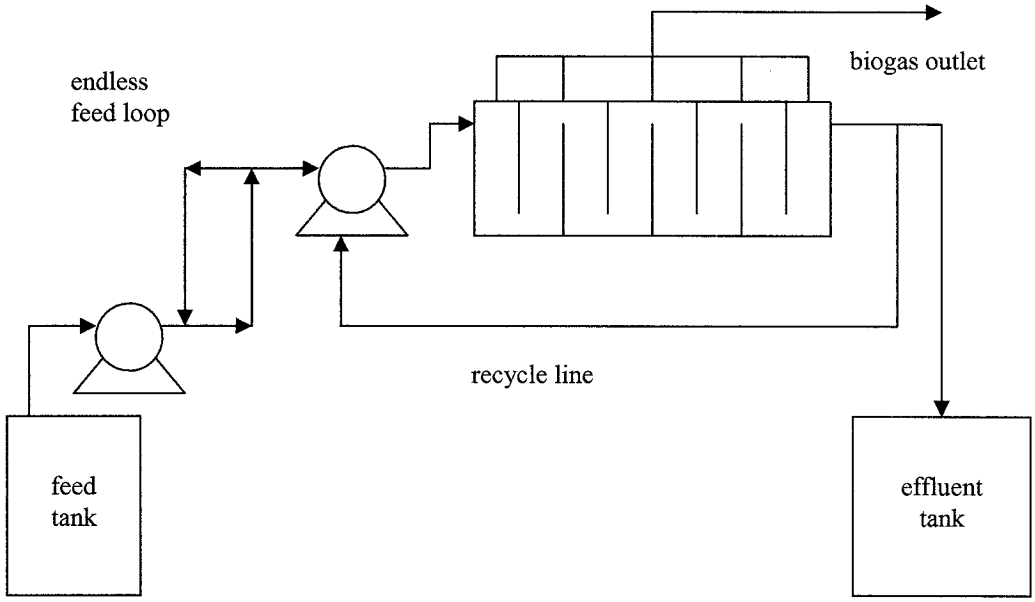

Figure 3.2: Reactor set-up schematic

The wastewater first flowed from the top of the downflow section of the first compartment, down through the first biomass bed and then up through the biomass bed in the upflow section of the compartment. The wastewater then spilled over the upcoming baffle into the following compartment and repeated the process, eventually exiting from the exit port at the top of the upflow section of the fourth compartment. The recycle fraction was drawn from the top sample port in the final upflow section. The reactor effluent exited through the outlet port and flowed to a U-tube which served to maintain the anaerobic conditions within the ABR and was accumulated in effluent tanks. The biogas produced within the ABR was channelled though the collection manifold to the wet tip gas meters for measurement of its volume. Liquid and solid samples required for

the various analytical tests were collected through sample ports located at the top and bottom portions of each of the upflow and downflow sections of the compartments (Fig. 3.3).

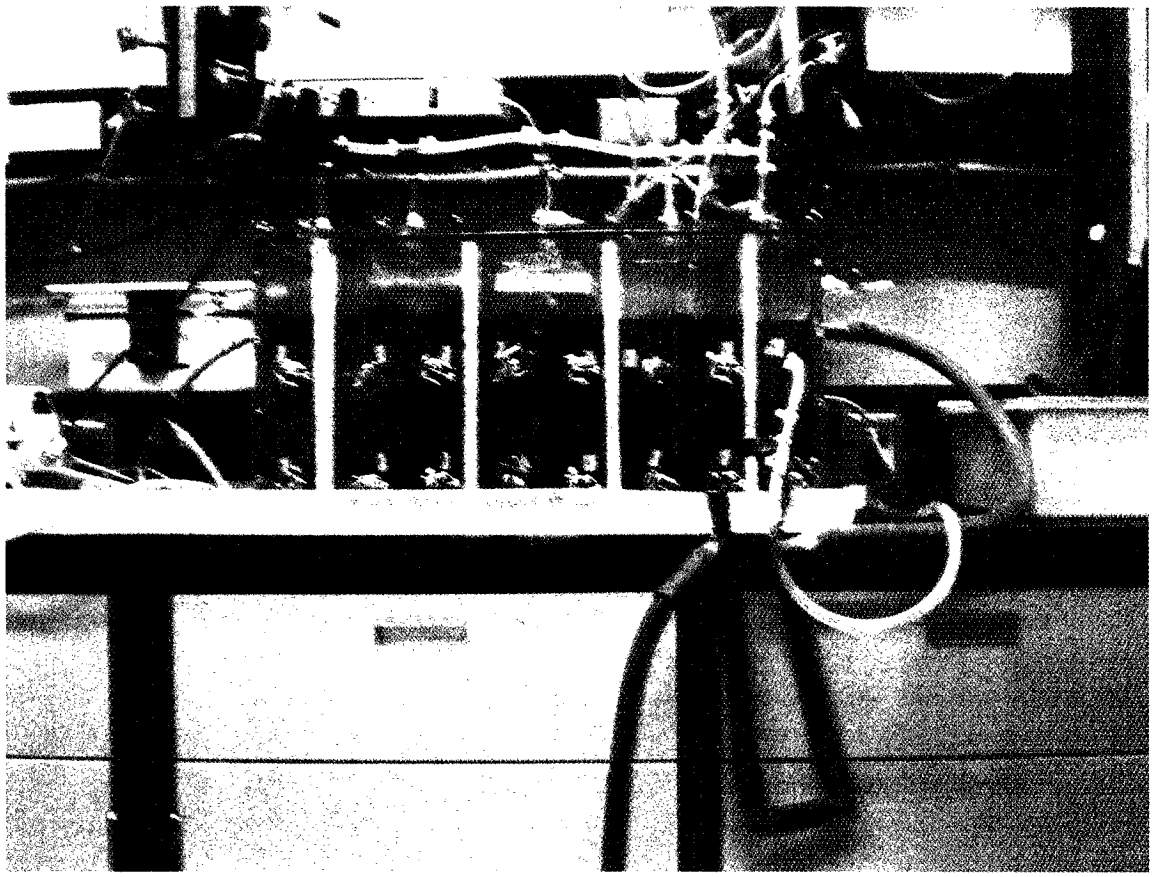

Figure 3.3: Reactor set-up

3.2 Mixing Study:

One objective of this study was to apply the model presented by Xing et. al (1991) to describe the performance of Hybrid Anaerobic Baffled Reactors (HABR) treating molasses wastewater to an ABR treating ADF. One of the main assumptions of the model evaluated by Xing et al. was that the HABR acted hydrodynamically as a group of CSTR-in-series. Since the ABRs used in this present study differed from the HABRs used by Xing et al. the hydrodynamic characteristics of the ABR were tested before proceeding to the biological phase of testing.

An ABR filled with only water was run at various HRT with a feed of pure water. The feed water was then replaced with a diluted solution of Rhodamine tracer. The outlet tracer concentration was then monitored with time and measured using a fluorometer and a calibration curve in order to determine the number of ideal CSTR-in-series that could be used to represent the reactor.

F curves of the type used by Levenspiel (1999) were then created. The output **F** curve from a series of N ideal CSTR in series can be described by the equation:

$$\mathbf{F}=1-e^{-N\theta}\left[1+N\theta+\frac{(N\theta)^2}{2!}+\ldots+\frac{(N\theta)^{N-1}}{(N-1)!}+\ldots\right] \qquad \text{Eqn. 14}$$

The **F** curve is the dimensionless form of the effluent concentration curve. The dimensionless value of **F** is the normalized concentration and is calculated from the step tracer concentration and the value of the effluent concentration at time t. The value of θ, which is a unit of dimensionless time, is calculated from the HRT and t. In other words:

$$\mathbf{F}=\frac{C_t}{C_{tracer}} \qquad \text{Eqn. 15}$$

$$\theta=\frac{t}{HRT} \qquad \text{Eqn. 16}$$

where: N = number of ideal CSTR in series

C_t = outlet tracer concentration at time t

C_{tracer} = step input tracer concentration

t = time since the step tracer input

and, HRT = hydraulic retention time.

Plotting the change of **F** with θ creates the experimental **F** curve. The resulting experimental **F** curve can then be compared to the CSTR in series **F** curves to determine whether or not the CSTR in series model can accurately describe the ABR. The theoretical **F** curves were then superimposed on the experimental **F** curves. Then, for the theoretical curves having the closest fit, an R^2 value was calculated from:

$$R^2 = \frac{RSS_{cfm}}{TSS_{cfm}} = \frac{\sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \qquad \text{Eqn. 17}$$

where: RSS_{cfm} = residual sum of squares corrected for the mean
TSS_{cfm} = total sum of squares corrected for the mean.
$\bar{y}$ = average value of y (in this case **F** from the mixing study)
$\hat{y}$ = value predicted by the model
and, y_i = value of y obtained experimentally,

and where R^2 represents the proportion of the total variation about the average that can be explained by the model.

Since there are changes in the mixing regime as the flowrate changes the concern before commencing testing was that, at low flowrates, the ABR would behave at near-plug flow conditions and that the model assumption that each of the compartments behaved as completely mixed although the series of compartments promoted plug flow conditions, would not hold. If the CSTR-in-series model could be held as valid, COD samples could be taken from the upper sample port in each of the upflow sections and this single COD sampling location could be considered to represent the COD within the entire compartment. In order to determine whether the reactor would behave as predicted by Xing et al. (1991), tests were carried out at the extremes of the anticipated flow range as well as at the centre, that is at HRTs of 36 h, 6 h and 1 h.

3.3 Biological Treatment:

For the biological phase of the study, each ABR was placed on a lab bench located in a temperature-controlled room (34 ± 2°C). In order to determine the minimum HRT, or maximum OLR achievable, each ABR was initially run at a long HRT which was decreased with time. This stepwise reduction in HRT was found by Barber and Stuckey (1999) to be the most efficient way to acclimate the biomass to an increased loading rate. In the acclimation phase, both ABRs were set to recycle and the flowrate was ramped up over a four week period from an initial HRT of 80 h to their respective first steady state HRT (39 h without recycle and 36 h with recycle). The ABR that was to

be run without recycle was run with recycle during start-up. Starting up the reactors with recycle diminished the toxicity of the feed to unacclimated biomass.

In the case of the ABR without recycle, the reactor was initially run at an HRT of 39 h, while the ABR with recycle was initially run at an HRT of 36 h. The ABRs were considered to be at steady state when the outlet VFA concentrations remained constant (± 10%) for three consecutive days. Each steady-state condition was maintained for no less than 3 hydraulic retention times. In the case of HRT less than one day, the reactors were maintained at steady state for three consecutive days before increasing the feed rate (decreasing the HRT). At steady-state, COD samples were taken from the port at the top of the upflow section of each compartment (one measurement for each compartment), VFA samples were taken from these same ports to create VFA profiles. The suspended solid content of the effluent was monitored daily.

Table 3.1: Summary of steady state conditions tested

ABR	HRT (h)	OLR (g COD/L reactor·d)
without recycle	39	4.3
	27	6.2
	20	8.4
with recycle	36	4.1
	24	7.0
	20	8.4
	17	9.9
	14	10.8

3.4 Feed Composition:

The carbon source in the synthesized ADF wastewater was ethylene glycol. The COD of concentrated UCAR XL 54 ADF was 700 – 800 g/L. All experiments were conducted at 1% ADF by volume (i.e. 7000 mg COD/L). Required nutrients and buffering capacities were added as shown in Table 3.2 to give a COD:N:P ratio of

100:5:1 this is an excess of nutrients for anaerobic systems where the optimum ratio is 700-750:5:1 (Droste, 1997) Yeast extract was used to meet micronutrient requirements and excess buffer capacity was provided.

Table 3.2: Feed composition

Component	Amount
ADF	10 mL/L
NH_4HCO_3	1.6 g/L
$NaHCO_3$	3.63 g/L
$KHCO_3$	2.78 g/L
$(NH_4)_2SO_4$	0.40 g/L
K_2HPO_4	0.21 g/L
KH_2PO_4	0.16 g/L
Yeast extract	0.08 g/L

A feed concentration of 1 % (v/v) ADF was chosen based on previous studies with ADF treatment in anaerobic reactors. Pham (2002) found when the anaerobic granular biomass used in this current study was fed a feed solution of 1.2 % ADF, the biomass exhibited toxicity effects. Further, Pham's Anaerobic Toxicity Tests showed that a concentration of 1 % ADF was not inhibitory to the granular anaerobic biomass used in this study.

3.5 Biomass Characterization:

3.5.1 Settling Tests:

Biomass samples were taken from each compartment of each reactor at the end of the run period for determination of its VSS and settling characteristics. These results were then compared to that of the seed sludge. Biomass settling velocities were determined based on the procedure described by Andras et al. (1989). A 7 mL biomass sample was placed in a glass upflow velocity test tube (L = 20 cm, ID = 19 mm). Warm water (35°C) was pumped through the tube for 5 minutes at successively increasing flowrates. The fractions of biomass overflowing from the tube were collected on

Whatman® 185 mm diameter, grade 1 filter papers (11 μm pore size) and settling curves were determined by plotting the cumulative TSS washout against upflow velocity. The settling velocity for the granular biomass, υ_{50}, was considered to be the velocity at which 50 % of the biomass had washed out. The results obtained for the end-run biomass samples were then compared to results obtained for the seed sludge.

3.5.2 Acetoclastic Activity Tests:

Acetoclastic Activity Tests (AAT) were performed at various times through the run-period, at the completion of steady state operation in order to determine the evolution of biomass acetoclastic activity. The AAT is based on known procedures (Speece, 1996) but the method was modified to suit laboratory conditions. It was found that, due to the excellent settling properties of the anaerobic granules, it was difficult to accurately pipet a biomass sample, and in the time required to do so, the biomass came in contact with air regardless of nitrogen flushing and the resulting tests showed little to no activity. Therefore, 10 mL samples of biomass were measured and transferred anaerobically directly from the reactor to nitrogen flushed 160 mL serum bottles using a modified wide mouth syringe. The bottle contents were then diluted with 40 mL of reactor supernatant to give a biomass concentration of approximately 7 g VSS/L. The sealed and capped serum vials were shaken overnight at 35°C to allow the VFA levels within the bottles to drop to zero. 0.2 mL of acetic acid stock solution 0.2 mL (see Table 3.2) was injected into each bottle to give initial acetic acid concentrations of approximately 1500 mg/L. Acetic acid consumption rates were monitored over time to determine its consumption rate.

Table 3.3: Acetic acid stock solution for acetoclastic activity tests

Component	Concentration (g/L)
Ammonium acetate	31.3
Potassium acetate	41.4
Sodium acetate	46.2
Glacial acetic acid	16.8

3.6 Analytical Methods:

3.6.1 COD Analysis:

COD analysis was performed using the closed reflux colorimetric technique (APHA, 1985). A Perkin-Elmer spectrophotometer was used to measure the light absorbance at 600 nm of the prepared COD samples. COD samples were taken from the upper sample port at the effluent end of each compartment at each steady state. These samples were then centrifuged for 10 minutes at 10,000 rpm. The supernatant was then drawn off to determine the soluble COD at the exit of each compartment. COD tests were performed in duplicate and where severe discrepancies with these measurements occurred, a third sample was analysed.

3.6.2 VFA Measurements:

VFA concentrations were determined using the internal standard method described by Ackman (1972). Using a Hewlett-Packard 5840A gas chromatograph with a flame ionisation detector maintained at 350°C and a Chromosorb 101 packed column (304.8 cm Find the multiplication sign 2mm ID, 80/100 mesh size) in an oven set at 180°C with an injection temperature of 250°C. The flowrate of the formic acid saturated helium carrier gas was 15 mg/min. VFA samples were centrifuged at 5000 rpm for 2 minutes in a microcentrifuge, and the supernatant was diluted with an equal volume of an internal standard containing 1000mg/L isobutyric acid prior to injection.

3.6.3 VSS and TSS Determination:

The total and volatile suspended solids contained in effluent samples and in biomass samples were determined using procedures outlined in Standard Methods (APHA, 1985). Biomass samples were placed in a pre-ashed, preweighed crucible and dried in a 108°C oven overnight and the dry weight was recorded. The dry sample was then ashed in a 550°C muffled furnace for 20 minutes. The difference between the dry weight and the crucible weight represented the TSS portion of the biomass, while the difference between the dry and ashed weights represented the VSS portion. Effluent samples were filtered through GF/C glass filters (VWR Canlab) and the filters were dried then ashed for TSS and VSS determination.

Chapter 4

Results and Discussion

4.1 Mixing Study:

As previously mentioned, one objective of this study was to determine whether or not the model utilized by Xing et. al in their 1991 study of HABR performance could be used in an ABR study. Since there are changes in the mixing regime as the flowrate changes the concern before commencing testing was that, at low flowrates, the ABR would behave at near-plug flow conditions and that the model assumption that each of the compartments behaved hydrodynamically as completely mixed, although the series of compartments promoted plug flow conditions, would not hold. If the CSTR-in-series model could be held as valid, COD samples could be taken from the upper sample port in each of the upflow sections and this single COD sampling location could be considered to represent the COD within the entire compartment. In order to determine whether the reactor would behave as predicted by Xing et al. (1991), tests were carried out at the extremes of the anticipated flow range as well as at the centre, that is at HRTs of 36 h, 6 h and 1 h.

A mixing study was carried out in an ABR containing only water using a step input of Rhodamine tracer and by measuring the variation of the tracer concentration at the outlet of the reactor with time over 2.5 hydraulic retention times. At the end of each test the tracer concentration at the outlet of the reactor had stabilized to a minimum of 95 % the inlet tracer concentration for the test at 36 h HRT, at 96 % for 6 h HRT and at 97 % for 1 h HRT.

Originally, it was planned to use a pulse injection of Rhodamine tracer, as Grobicki and Stuckey (1992) used this method. However, due to the large amount of tracer required in a reactor of this size (30.8 L working volume) to maintain the Rhodamine tracer in the detectability limits of the spectrophotometer (0.1 mg Rhodamine/L), either a large quantity of tracer would have to be injected, or a smaller quantity of more concentrated tracer would have to be used. Neither of these options proved viable. At the low flowrates involved in this study (0.8 L/h for a 36 h HRT) a one shot injection of 20 mL of 100 mg Rhodamine/L caused an undue amount of mixing within the first compartment. The tracer entered the first compartment faster than the

feed, struck the downflow baffle and mixed outward. Most of the downflow section of the first compartment turned pink immediately. This test also proved to be at too low a tracer concentration to achieve a reliable concentration profile with time. The second option also proved impossible. At high concentrations (10 mL of 20,000 mg Rhodamine/L), the tracer did not mix well with the water within the reactor. A density gradient formed, where the tracer immediately sank to the bottom of the reactor, forming a blanket, which did not mix readily with the surrounding water. For these reasons, it was decided to use a step injection of tracer. The tracer was mixed with the feed water to create a 5 mg Rhodamine/L solution which was then fed into the inlet of the reactor. The outlet tracer concentration was then monitored with time. The concentration of the tracer was measured using a fluorometer and a calibration curve.

Residence time distribution (RTD) **F** curves were created from the Rhodamine concentration with time data collected for HRTs of 36 h, 6 h and 1 h.

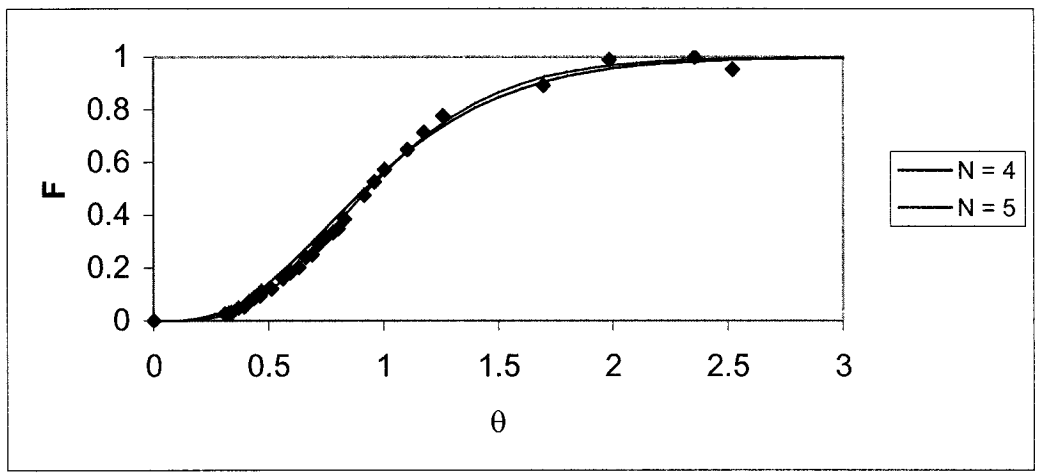

Figure 4.1: **F** curve for 36 h HRT with N = 4 and 5 models superimposed

Figure 4.1 represents the mixing study carried out at a HRT of 36 h where unitless concentration **F** is plotted against unitless time θ, and has superimposed upon it the theoretical models for N = 4 CSTR-in-series and the theoretical model for N = 5 CSTR-in-series. As can be seen from this figure, either model could describe the mixing within the ABR under these conditions.

As demonstrated in Table 4.1, the R^2 (1.02) indicates that the CSTR in series model where N = 5 would have a marginally better fit than the model where N = 4 (R^2 = 0.94). However, a model where the number of CSTR in series is equal to the number of compartments (i.e. N = 4) is still plausible.

Similar comparisons of the mixing study results with theoretical CSTR in series model predictions were carried out for the 6 h and 1 h HRT mixing test and can be seen in Figures 4.2 and 4.3.

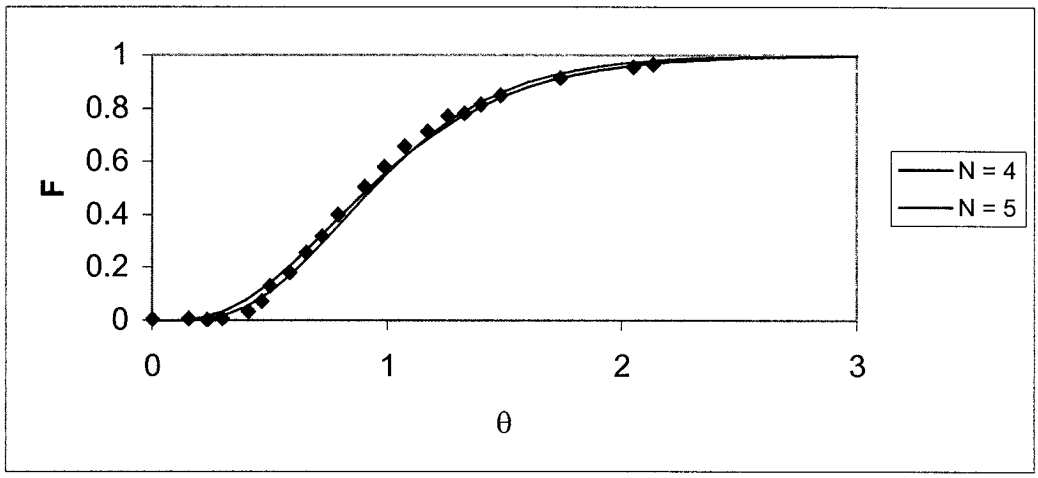

Figure 4.2: **F** curve for 6 h HRT with N = 4 and 5 models superimposed

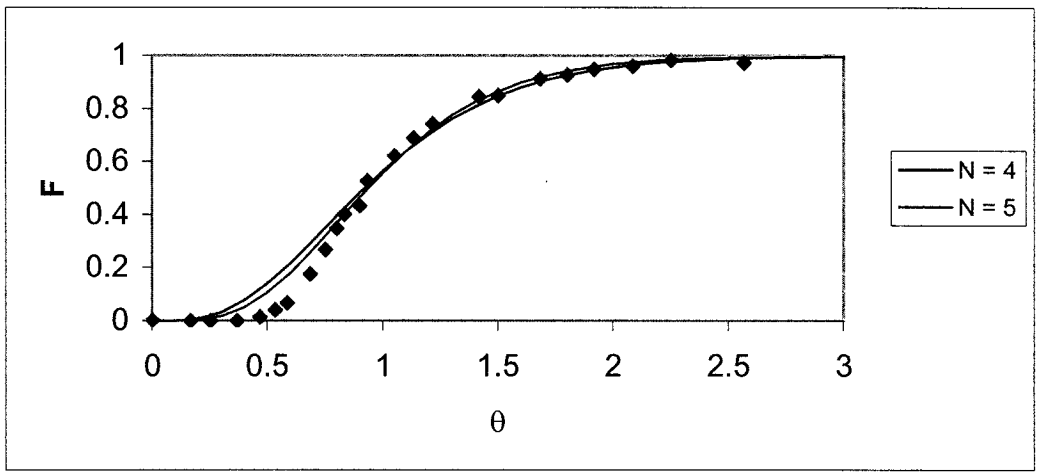

Figure 4.3: **F** curve for 1 h HRT with N = 4 and 5 models superimposed

Table 4.1: Comparison of model fits for mixing tests

	R^2		
F curve model	36 h HRT	6 h HRT	1 h HRT
N = 4	0.94	0.93	0.85
N = 5	1.02	1.01	0.92

Table 4.1 shows the R^2 values for the for each of these RTD studies and shows that although the N = 5 model provides a slightly better fit than the N = 4 model in all cases (1.02 vs. 0.94 at 36 h HRT; 1.01 vs. 0.93 at 6 h HRT; and 0.92 vs. 0.85 at 1 h HRT) it is never implausible that N = 4 and it is reasonable to describe this system as CSTR-in-series with N equal to the actual number of compartments for all HRTs studied. Furthermore, although the **F** curve model shows some deviation from the data at θ less than 1, at θ greater than 1 (that is at times greater than 1 HRT) the model fit is adequate.

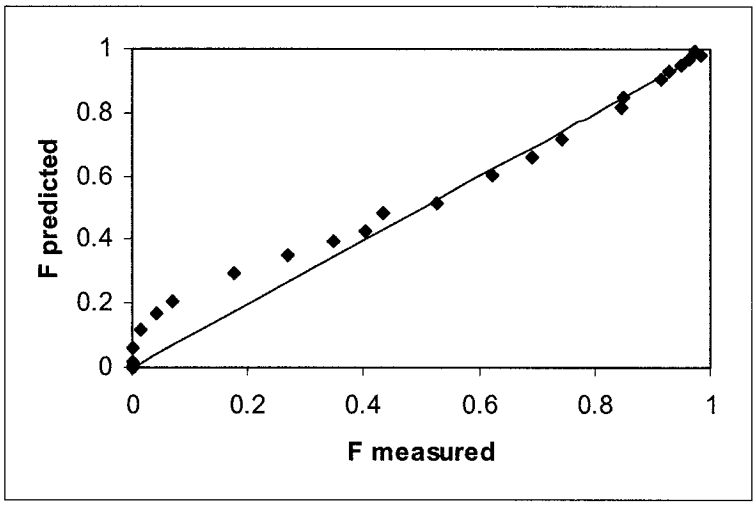

Figure 4.4: Residual plot for N = 4, HRT = 1 h

Residual plots present the difference between the values predicted by a model and the actual values measured during testing. If a model had a perfect fit, the residual plot would have a slope of 1. Any deviation of the model from the data is visible in a residual plot, and ideally the residual points would be randomly distributed around the line of slope 1. RTD studies are by their very nature correlated (i.e. the value of one measurement will depend on the value of the previous measurement) therefore a residual plot would be expected to be correlated and will not show the random distribution about 1. Figure 4.4 shows the residual plot for the N = 4 model at a 1 h HRT which is the residual plot which shows the greatest deviation from the theoretical perfect fit (See Appendix A). It can be seen that although the model varies significantly from the data for θ less than 1 (that is at F measured less than 0.5), at θ greater than 1 the variation of the model from the data is minimal. Therefore, it is reasonable to assume that an ABR may be represented as a series of CSTR-in-series.

Levenspiel (1999) points out that in the case of CSTR in series with recycle and throughflow, where the recycle is relatively rapid compared to the throughflow, the system as a whole acts as one large CSTR. The model used by Xing et al. accounts for this effect and therefore, since without recycle the ABRs can be said to behave as 4 CSTR-in-series, then the model used by Xing et al. should also account for the hydraulic effects of the recycle. Further, these results agree with those of Grobicki and Stuckey (1992). In their study, Grobicki and Stuckey concluded that reactors operated with biomass and gas mixing were even better suited for CSTR-in-series characterization wherein the number of theoretical compartments was equal to the actual number of compartments than were reactors tested without biomass. It was found that although the presence of the biomass in itself increased the dead space within the reactor (biological dead space), the increased mixing caused by the evolution of gas within the active reactor decreased the hydraulic dead space and compensated for the presence of biological dead space. Given the results of the mixing study in view of the results put forward by Grobicki and Stuckey it is reasonable to assume that the ABRs may be represented by a CSTR-in-series model where the number of theoretical CSTRs is equal to the number of compartments in the ABR and further, it is reasonable to assume that each compartment of the ABR will behave as a CSTR and that a single sample may be held representative of the concentration within the entire compartment.

4.2 Biological Treatment:

4.2.1 Start-up and Timeline:

As mentioned previously, during the biological treatment phase of this study two bench-scale ABRs were operated in continuous mode and each of these four compartment reactors were inoculated with 10 L of anaerobic granular biomass. The 10 L of biomass were separated evenly between each of the four compartments within each reactor (i.e. 2.5 L/compartment) and although both reactors were equipped with an internal recycle line set at a 6:1 recycle ratio, only one reactor was operated with recycle, while the other was operated without. The simulated ADF waste was initially fed to the ABRs at a relatively long HRT to allow acclimation of the biomass, and then the HRT was stepped down to achieve a succession of HRT quasi-steady states. Steady state

operation was determined to be a series of 3 HRT (or 3 days, whichever was longer) where the effluent VFA concentrations remained constant. Liquid and solid samples required for the various analytical tests were collected through the sample ports located at the top and bottom portions of each of the upflow and downflow sections of the compartments for each steady state. Figures 4.5 and 4.6 illustrate the timeline of the study and show the COD removal efficiency obtained at each steady state for each ABR.

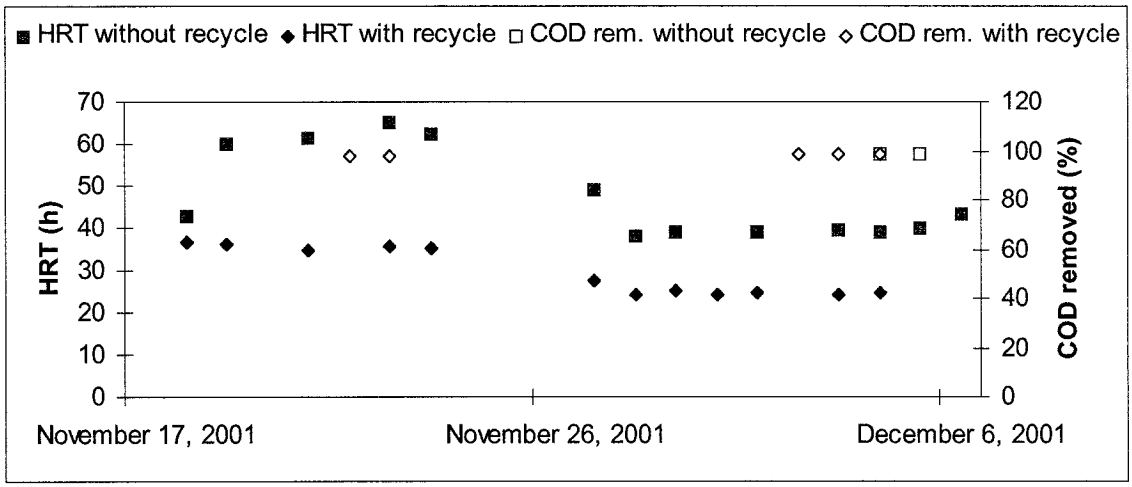

Figure 4.5: HRT loading timeline and COD removal efficiency in the first phase of testing

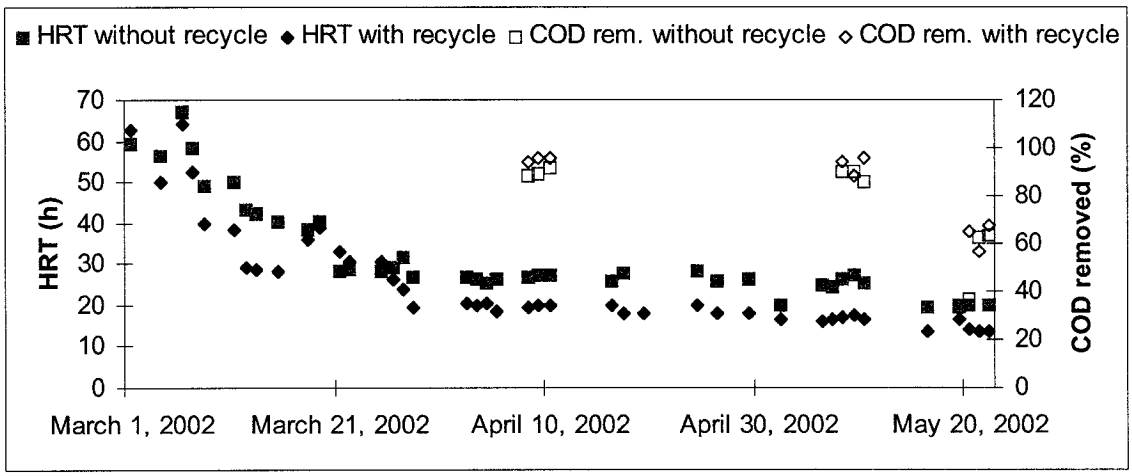

Figure 4.6: HRT loading timeline and COD removal efficiency in the second phase of testing

During the experimental period, the ABRs were shut down for three months, that is to say that all pumps were shut off and the reactor allowed to sit undisturbed at room temperature from Dec. 6, 2001—Mar.1, 2002, in order to determine whether they could be restarted with ease. Upon re-startup, the ABRs were brought back to the HRT of the previous steady state and the outlet COD was measured in order to determine the COD removal. The COD removal efficiencies after re-startup were similar to those before the shut down indicating that ABRs treating 1% ADF may be shut down for a period of up to 3 months and then restarted with ease.

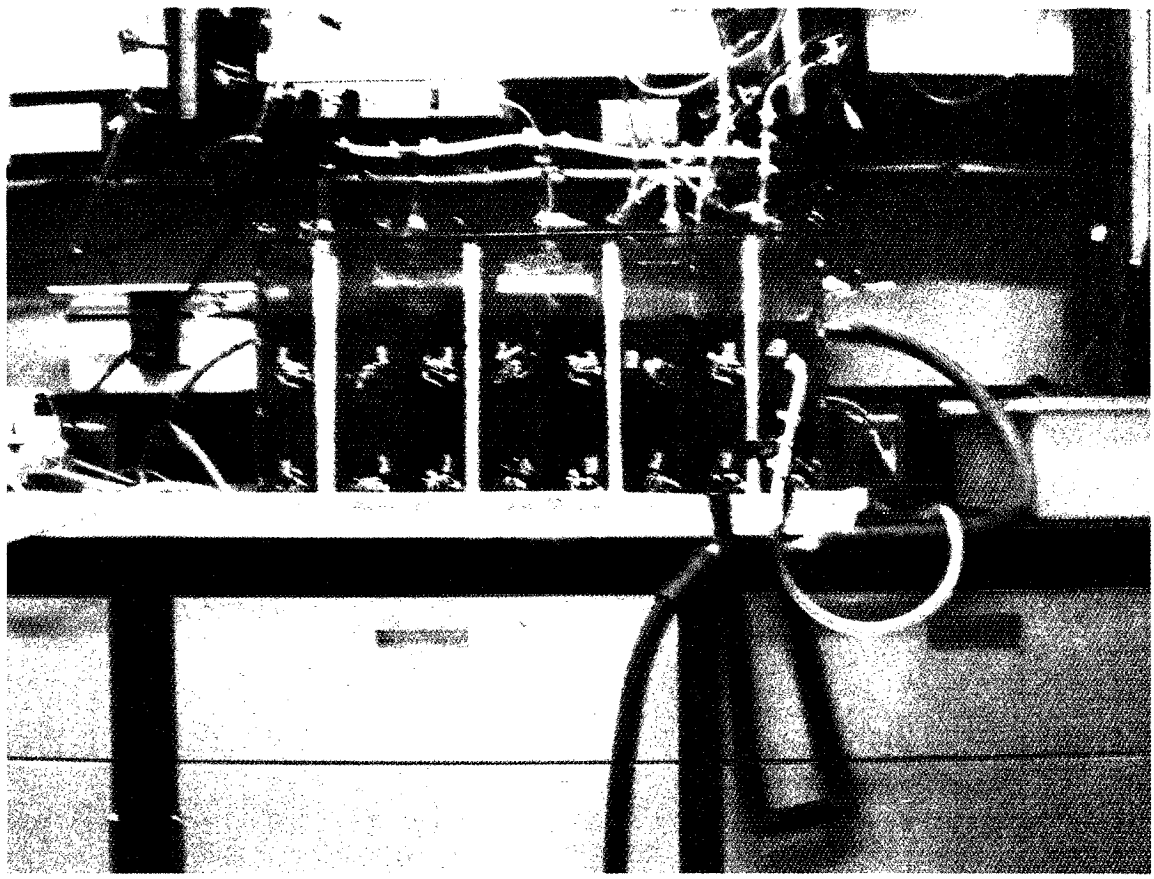

Figure 4.7: Reactor set-up

4.2.2 COD Profiles:

Since mixing studies indicated that the ABR behaved as CSTR-in-series, COD profiles from compartment to compartment were created to show the change in COD as substrate moved through the ABRs. The COD reported for each compartment was the average of two samples taken from the effluent end of that compartment. This was then

considered to be the influent for the following compartment. In the case of the ABR with recycle, the effluent from compartment 4 was also the portion of the reactor contents that was recycled back to the inlet and therefore affected the concentration of the liquid entering into compartment 1.

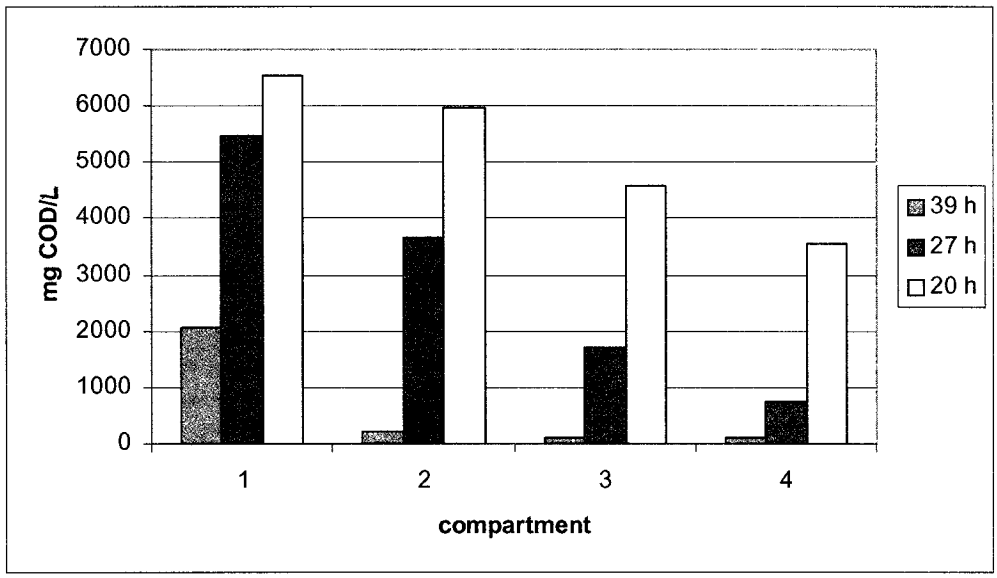

Figure 4.8: COD profile, no recycle

When the ABR was operated without recycle (Figure 4.8), the COD decreased steadily as the wastewater moved through the reactor, from compartment 1 to compartment 4 for each HRT tested. For example, at an HRT of 27 h, the wastewater which entered the reactor with a COD of 7000 mg/L, had a COD of 5500, 3600, 1700, and 700 mg COD/L at the outlets of compartments 1, 2, 3 and 4 respectively. It is also important to note that, as the HRT was shortened (OLR increased), the COD concentrations within each compartment increased accordingly. For example, in compartment 1 COD concentrations increased from 2000 mg/L at an HRT of 39 h to 5500 mg/L at an HRT of 27 h and finally to 6500 mg/L at an HRT of 20 h. This same trend occurred in each compartment with decreasing HRT.

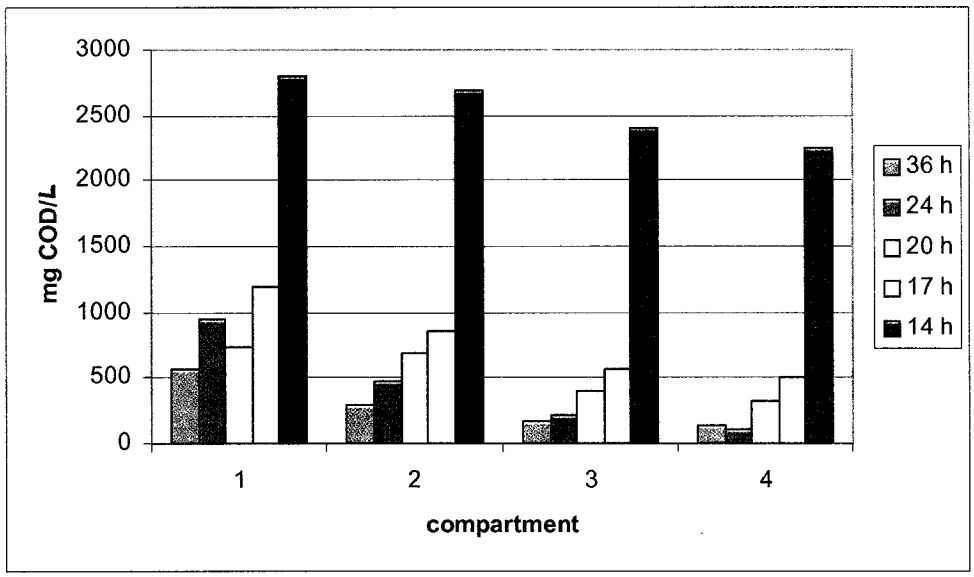

Figure 4.9: COD profile, with recycle

For ABR operated with recycle, (Figure 4.9) the same phenomenon was also observed, but to a lesser extent. For example, at an HRT of 24 h, the COD in each compartment of the ABR with recycle decreased from the 1000 mg/L in compartment 1 to 100 mg/L in compartment 4, a decrease by a factor of 10, while in the reactor without recycle at a HRT of 27 h the decrease between compartments 1 and 4 was by a factor of about 8. While the CODs decreased by about the same factor in both cases, the magnitude of the COD concentration is much higher in the ABR without recycle indicating improved performance with recycle. What is also visible from these two figures is that for all HRTs evaluated, the COD concentration in compartment 1 as well as for all subsequent compartments was always lower for the ABR operated with recycle than for the ABR operated without recycle at similar HRTs. This is the recycle dilution effect. The low COD out of the fourth compartment acted to dilute the relatively high COD of the feed wastewater at the 6:1 recycle to feed ratio used in the study.

4.2.3 COD Removals and VFA Profiles, Without Recycle:

The compartment to compartment COD profiles in themselves do not provide great insight into the operation of the reactors; therefore it is more useful to look at ABR operation from the viewpoint of the amount of COD removed. Given that the influent

COD concentration was constant at 7000 mg/L in all experiments, the COD removal efficiency can be calculated from:

$$\% \text{ COD removed} = \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100\ \% \qquad \text{Eqn. 18}$$

where COD_{in} and COD_{out} are the COD concentrations into and out of each compartment. In calculating the COD removal efficiency for compartment 1, COD_{in} is the influent wastewater concentration of 7000 mg/L and the COD_{out} is the COD concentration of the sample taken from compartment 1. Since each compartment can be said to operate as a CSTR, the concentration within each compartment should be the same as the concentration of the effluent of that compartment. Then, the COD_{out} for compartment 1 becomes COD_{in} for compartment 2 and so forth through to compartment 4.

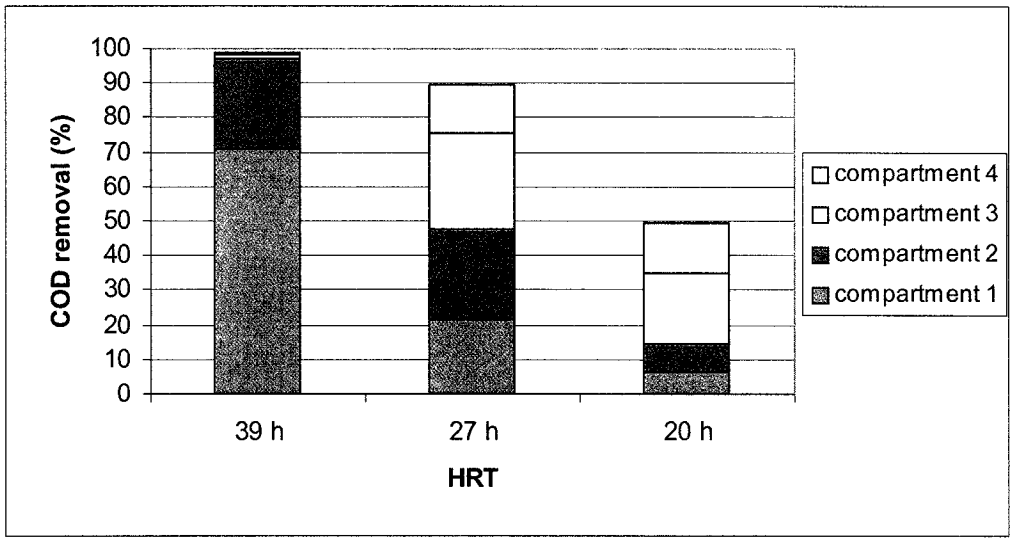

Figure 4.10: COD removal efficiency at the outlet of each compartment, no recycle

Figure 4.10 shows overall as well as compartment to compartment COD removal efficiency versus HRT for the ABR without recycle. Here, the COD shown is cumulative, with COD_{in} equal to the influent concentration in all cases. In the case of the ABR without recycle, overall COD removal at the longest hydraulic retention time (HRT = 39 h) was very high and 98.7 % COD removal was achieved. However, what is also noticed is that most of the COD removal occurred in the first compartment (71 %) and 26 % in compartment 2. Less than 2 % of the overall COD was removed in compartments 3 and 4. This indicates that the entire reactor volume was not being utilized to its full potential.

In fact, the last two compartments could have been completely removed without significant loss in removal efficiency. Because of the high COD removal in compartments 1 and 2, both the specific loading rate (g COD/ g biomass·d) and substrate concentration driving force in the latter compartments (3 and 4) were low resulting in a lower substrate utilization rate. This result is not unexpected, as Xing et al. (1991) noticed that nearly 80 % of the total COD removal occurred within the first compartment.

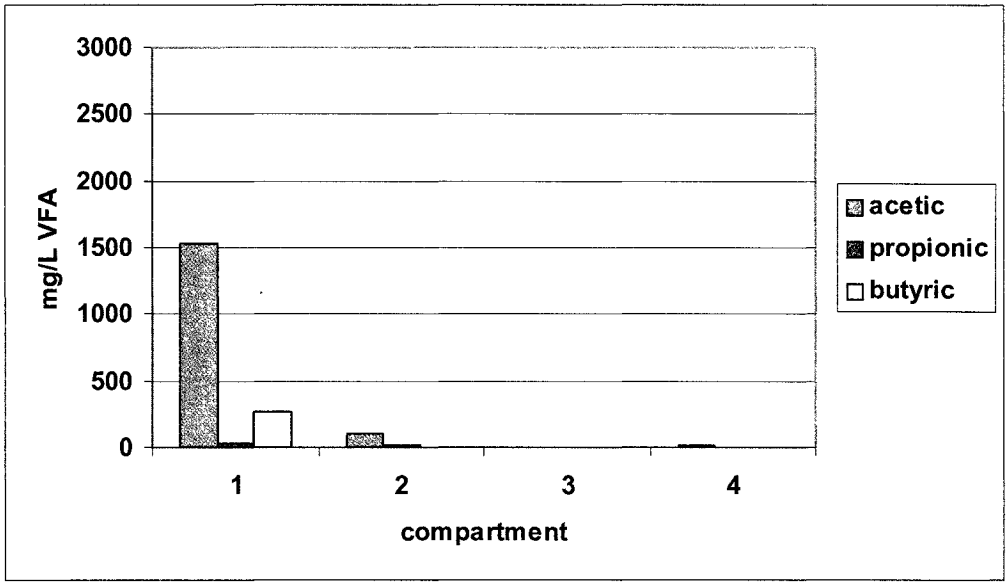

Figure 4.11: VFA profile at 39 h HRT, without recycle

At 39 h HRT, the acidification of the reactor contents in the first compartment was visible with an acetic acid concentration greater than 1500 mg/L (Fig. 4.11). Butyric acid was also present at low concentration (270 mg/L) but was consumed in compartment 2. The VFA concentrations in compartments 2 to 4 were negligible. This is in accordance with the COD drop that occurred primarily in the first and second compartments. Acidogenesis and methanogenesis occurred simultaneously within the first compartment and the remaining acids produced in the first compartment were consumed by methanogenic bacteria in the second compartment.

As the reactor was operated at shorter HRT, down to a 27 h HRT, it can be seen (Fig. 4.10) that the overall COD removal efficiency decreased to about 90 % but was equally spread out across all four ABR compartments. This indicates that as the ABR was stressed, the latter compartments played a greater role in terms of COD removal.

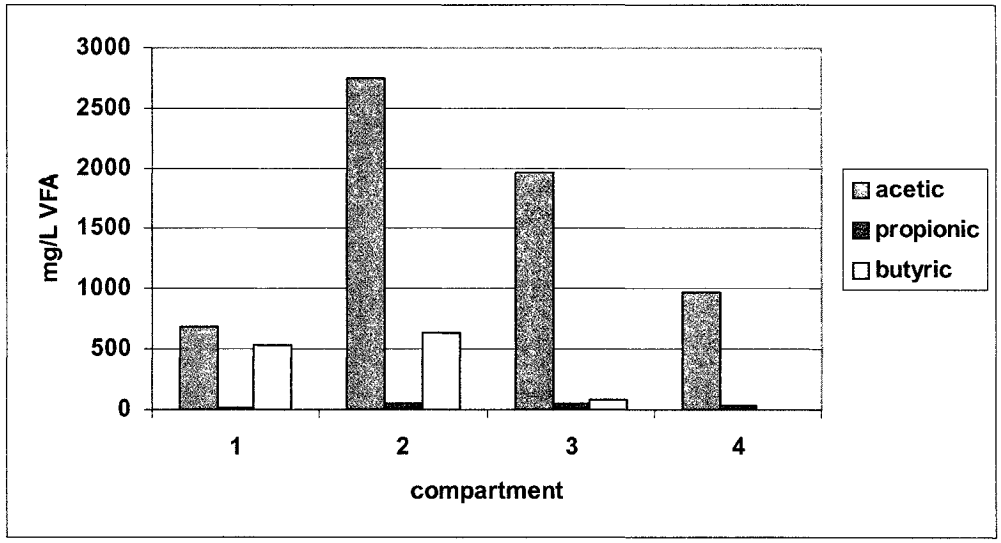

Figure 4.12: VFA profile at 27 h HRT, without recycle

At 27 h HRT, the final steady-state in the series at which acceptable COD removal occurred, acetic acid concentrations rose from the first to the second compartment indicating that the acidification had moved through the reactor, occurring not only in the first compartment as in the 39 h HRT (Fig. 4.12). Also, the rising concentrations of the longer chained butyric acid indicate that the anaerobic microbial consortia were beginning to be stressed (Speece, 1996). The overall acid concentrations in the reactor effluent were still less than 1000 mg/L.

At the shortest HRT tested (20 h) (Fig. 4.10), it can be seen that the ABR was operating at an overall COD removal efficiency of about 50 %, which was below the 70 % overall COD removal which was deemed to be the cutoff point for acceptable COD removal in this study. For this reason, the series of steady states was halted at this point. In this case, compartments 3 and 4 accounted for most of the COD removal (37 % overall removal) while compartments 1 and 2 accounted for about 13 % COD removal. The decreased removal in the first two compartments suggests that for these conditions acidogenesis was predominating in compartments 1 and 2 (no COD removal during acidogenesis) and that a more balanced anaerobic consortium with methanogenesis occurred mainly in the final two compartments. In order to verify this, it is necessary to look at the VFA profiles for this reactor (Fig. 4.13).

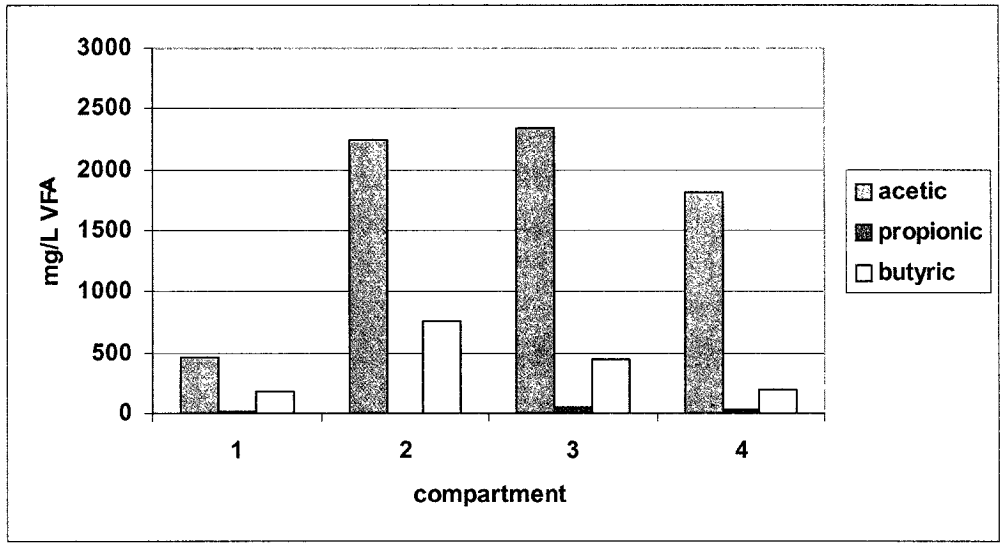

Figure 4.13: VFA profile at 20 h HRT, without recycle

At 20 h HRT, the rising concentrations of VFAs became truly apparent with effluent VFA concentrations well above 1500 mg/L. Since a rise in VFA concentrations entails a concurrent rise in the COD concentrations it is obvious why the COD removal rate had become unacceptable at this stage. The VFAs themselves now accounted for most of the COD seen in the effluent. The longer chained butyric acid concentrations had now risen to above 500 mg/L in three of the four compartments indicating the level of stress on the anaerobic biomass in those compartments (Speece, 1996).

It should be noted that although the acid concentrations increased within the ABR, due to buffering the pH within the reactor remained steady at 7.0 ± 0.2. Therefore, although pH is known to play a major role in reactor souring, the mere presence of the acids in a pH buffered solution clearly inhibits methanogenesis.

4.2.4 COD Removals and VFA Profiles, With Recycle:

In the ABR operated with recycle, the definition of removal within each compartment must be re-evaluated in order to avoid an artificially high COD removal rate within the first compartment due to the dilution effect of the recycle. The overall removal continues to be defined as in equation 18 but on the compartmental level however, the COD_{in} must be defined as the COD entering the first compartment and COD_{out} defined as the COD exiting that particular compartment, which in turn becomes

the COD entering the following compartment. The main ramification of this redefinition is that the COD into the first compartment is no longer considered to be the feed COD but the COD of the feed diluted by the recycle COD.

Having thus redefined the definition of compartmental COD removal, the removal for the ABR operated with recycle can now be more closely examined. In order to more readily compare the different HRT, the compartmental removals have been expressed as percentages of the overall removal accounting for the influent dilution. Overall, as can be seen in Fig. 4.14, the removal remained greater than 90 % for all steady-state conditions down to a HRT as short as 17 h. Thereafter the removal dropped below the acceptability limit of 70 % before an HRT of 14 h was reached. Therefore, recycle permitted acceptable treatment at shorter HRT and consequently at greater OLR than for an ABR without recycle.

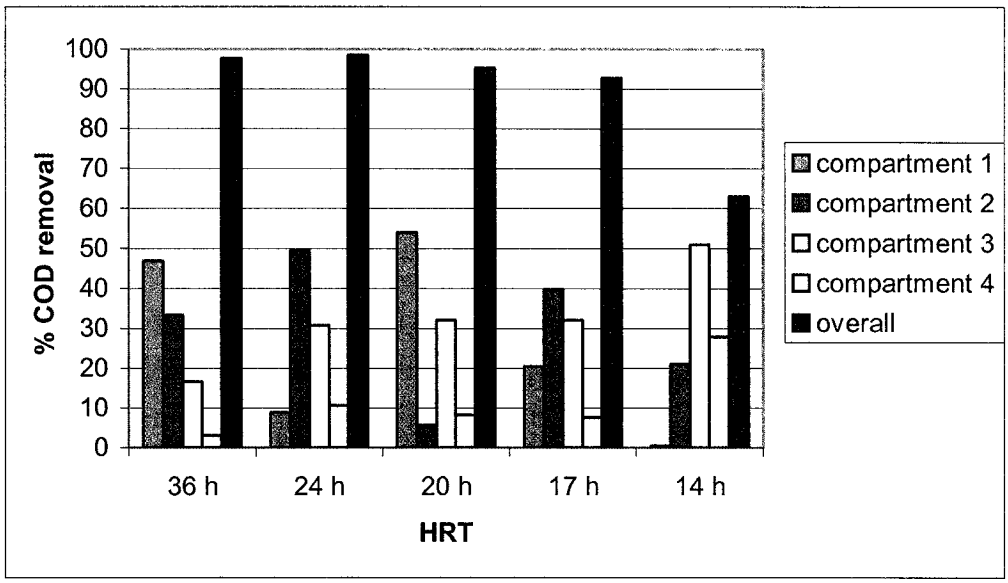

Figure 4.14: COD removal with recycle where compartmental removals are in percentages of overall removal accounting for dilution

On the compartmental level, at the longest HRT (36 h) the first compartment achieved removal of 47 % of the total COD removal while each successive compartment removed a smaller fraction of their influent COD (33% in compartment 2, 17% in compartment 3 and 3% in compartment 4.) This is expected since as the COD decreased in the preceding compartment the resultant COD driving force in the subsequent compartment was thus reduced, leading to a lesser removal efficiency. A look at the

VFA profile for an HRT of 36 h (Figure 4.14) reveals that the VFA concentrations within the reactor were inconsequential and as such did would not have affected COD removal efficiencies.

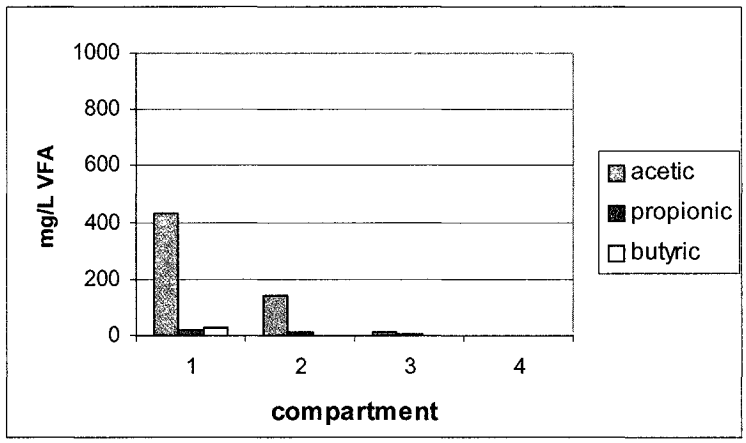

Figure 4.15: VFA profile at 36 h HRT, with recycle

As the HRT shortened from 36 h to 24 h, the removal efficiency within the first compartment diminished and subsequent compartments showed greater compartmental removal efficiencies.

At the subsequent steady state condition (24 h HRT) it can be seen that the removal took place at a latter part of the reactor. That is to say that the first compartment accounted for only 9% of the total COD removal while the second compartment accounted for 50%, the third compartment accounted for 31%, and the last compartment accounted for 11% of the total COD removal. This leads to the conclusion that the first compartment was more acidic than at the 36 h HRT and that in consequence the second compartment was in a better position to remove the COD. The VFA profile (Figure 4.15) supports this hypothesis. Within the first compartment the acetic acid concentrations had risen to above 600 mg/L with a butyric acid concentration creeping above the detectability limit. The butyric concentrations were no longer detectable at the outlet of compartment 2.

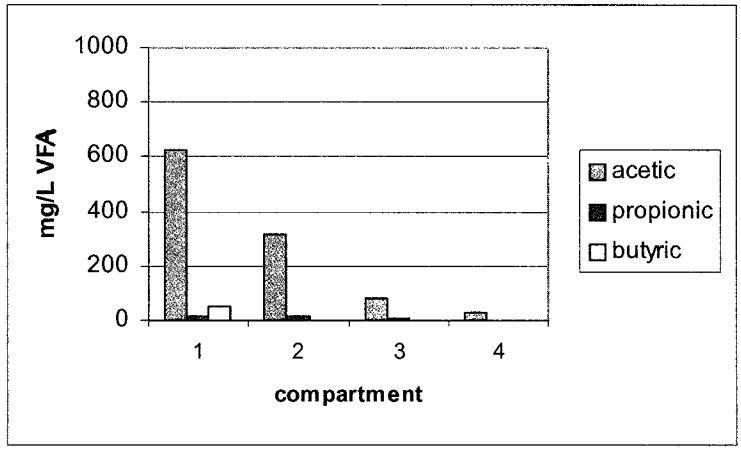

Figure 4.16: VFA profile at 24 h HRT, with recycle

At 20 h HRT, there was a substantial difference between the second (6%) and third (32%) compartment COD removals. This trend was visible for all three measurements taken at that steady state. It is unclear why this would occur. The measurement for the COD at the outlet of compartment 1 was so low, that it affected the removal efficiency calculation for compartment 2, making the removal efficiency calculated for compartment 1 artificially high (54%) and the removal efficiency calculated for compartment 2 artificially low. Although the reason for this is unclear, it is speculated that the COD samples from compartment 1 were contaminated with biomass that was improperly centrifuged. The 20 h HRT steady state was the first in which the biomass level in the first compartment was above the level of the upper sample port within that compartment, and as such, the samples for the compartment 1 COD necessarily contained biomass when extracted from the reactor. After extraction, the sample was centrifuged for 20 minutes at 10,000 rpm and decanted in order to remove the biomass from the sample. If the decanting was not appropriately performed, remaining biomass may have further degraded the COD in the sample before COD testing leading to artificially low readings for the COD concentration at the outlet of the first compartment and therefore accounting for the inconsistency in the COD profile and in the subsequent figures.

Although at the 20 HRT there was an incongruity within the COD removal efficiency profile, there was unfortunately no VFA profile available due to a temporary problem with the gas chromatograph.

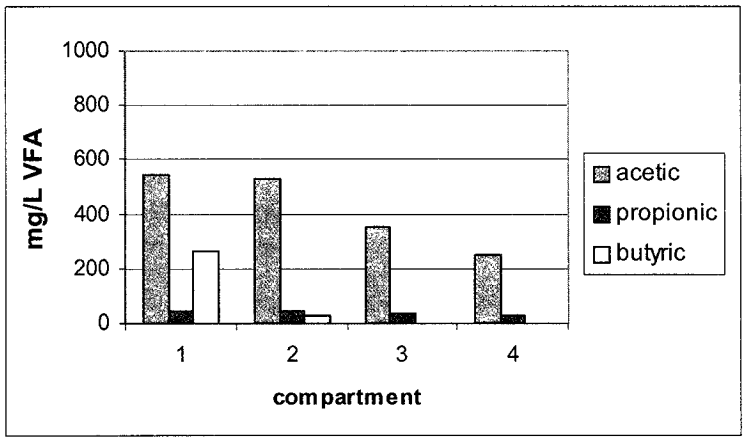

Figure 4.17: VFA profile at 17 h HRT, with recycle

At the fourth steady-state condition (17 h HRT) the shifting of COD removal to the latter compartments is again visible. The first compartment accounted for 20% of the overall removal while the second, third an fourth compartments accounted for 40%, 32% and 8% of the total removal respectively.

The VFA profile (Figure 4.16) indicates that the levels of biomass stress within the reactor were increasing. In particular, the first compartment was showing significant concentrations of butyric acid, said acid not being consumed until it entered the third compartment. Further the acetic acid concentrations were beginning to level off through the reactor, remaining above 400 mg/L at the reactor outlet. It must be noted that as the outlet acid concentrations increased (with the concurrent COD increase) the amount of acids returned to the inlet via the recycle increased. Therefore the increased acid concentrations in the first compartment was not entirely due to an increase in acidogenic activity, but was due in large part to the returning acid from the last compartment. Furthermore, as the HRT shortened, the amount of mixing within the reactor increased proportionally to (1 + R) times the influent flow rate. At these rates the reactor was moving away from the CSTR-in-series in favour of a single CSTR model.

As mentioned previously, once the reactor was operating at a 14 h HRT, the overall COD removal efficiency dropped to 63 %, which was below the acceptable removal level (Fig. 4.14). There was an increase in COD concentration from the first to the second compartment but this increase was well within the error associated with the measurements (see Appendix B), leading to a net 0 % COD removal efficiency in the first

compartment. Fifty percent of total COD removal occurred within the third compartment with the second and fourth compartments accounting for 21 and 28% of the total removal respectively. The majority of the removal had shifted from the first compartment at 36 h HRT to the second compartment at 24 h and 17 h HRT to the third compartment at a 14 hour HRT.

The reason for the drop in overall COD removal becomes obvious in view of the constant VFA profile from compartment to compartment for this steady-state condition where a CSTR-like profile is evident (Fig. 4.18).

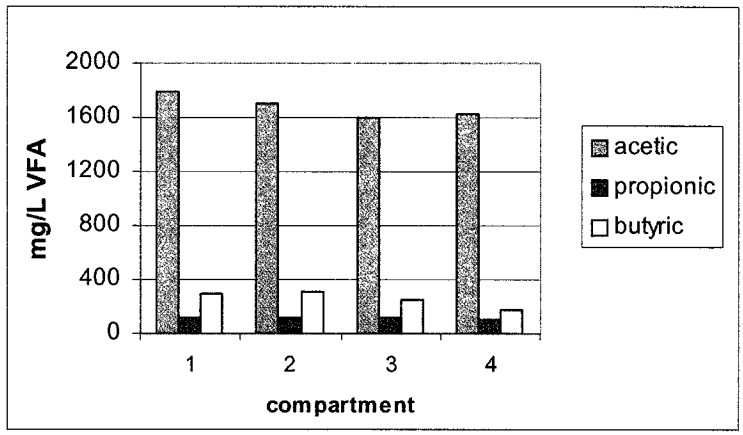

Figure 4.18: VFA profile at 14 h HRT, with recycle

It should be recalled that the volatile acids themselves carry an inherent COD as can be calculated from simple oxidation reactions:

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad \text{Eqn.19}$$

$$CH_3CH_2COOH + 7/2\,O_2 \rightarrow 3CO_2 + 3H_2O \qquad \text{Eqn. 20}$$

$$CH_3CH_2CH_2COOH + 5O_2 \rightarrow 4CO_2 + 4H_2O \qquad \text{Eqn. 21}$$

From equation 19, it can be seen that 60.0 g of acetic acid require 64.0 g of oxygen for complete oxidation; therefore acetic acid has a COD equivalence of 1.07g COD/g acetic acid. Similarly, from equation 20, 74.1 g propionic acid require 112.0 g of oxygen; therefore its COD equivalence is 1.51 g COD/g propionic acid. And further, 88.1 g of butyric acid require 160.0 g of oxygen; therefore its COD equivalence is of 1.82 g COD/g butyric acid.

Using these COD equivalences, it is possible to determine, for each set of COD/VFA profiles, what portion of the COD could be attributed to the VFA and in this way determine how far into the reactor the substrate penetrated before being acidified. From this, it was determined that for the ABR operated with recycle all the COD seen at the outlet of each of the compartments was due to VFAs and none due to the original ADF substrate as the totality of the substrate was acidified within the first compartment for all HRTs studied. Without recycle, substrate was acidified in compartment 1 at a 39 h HRT while substrate accounted for 69 % of the COD out of compartment 1 at an HRT of 27 h. At the final HRT of 20 h, the substrate accounted for 90 % of the COD out of compartment 1, 40 % of the COD out of compartment 2 and 30% out of compartments 3 and 4. This indicates that for the ABR operated without recycle there was insufficient acidogenesis occurring and that the decrease in removal to below acceptable levels was not due solely to insufficient methanogenesis as was the case in the ABR operated with recycle.

Throughout this study, results have been based on COD concentrations, however, as mentioned previously, waste stabilization occurs through methanogenesis and methane production is proportional to the COD removed. Biogas quality and quantity were measured periodically through the experimental period. The biogas quality was found to be of 60 ± 1% methane with a methane production of 0.32 ± 0.02 L CH_4/g COD_{rem}, which although less than the theoretical methane potential of 0.36 L CH_4/g COD_{rem} at 34°C (Speece, 1996) is not significantly different therefrom.

4.2.5 Biomass Accumulation:

In high rate reactors such as ABRs, the maximum rate at which the reactor can be run is limited by the rate of loss of the granular biomass used therein. As such, the accumulation of biomass within high rate reactors is of particular interest. In order to determine the amount of granular biomass within the ABRs, the volume of biomass contained within each compartment was monitored for each steady state using the graduations that were added to the outside of the reactors. Then, knowing the density of the biomass in terms of g VSS/mL of biomass it was possible to calculate the amount of biomass in the reactor on a VSS mass basis.

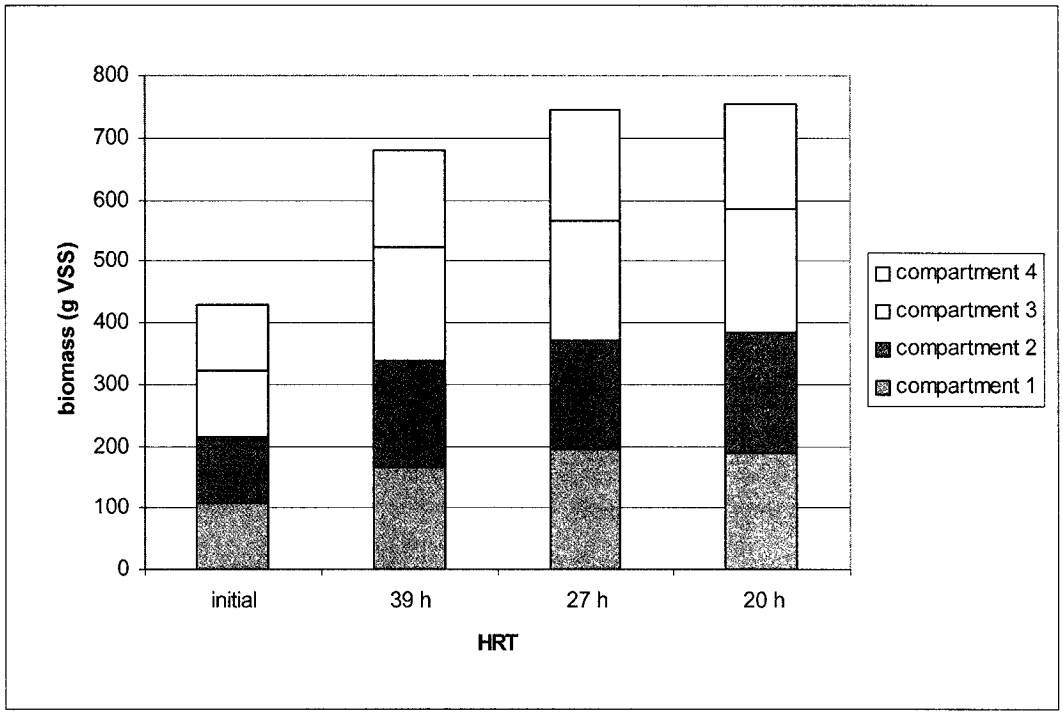

Figure 4.19: Biomass inventory across the reactor without recycle

What is immediately visible from figures 4.19 and 4.20 is that there was a net positive yield in both the ABRs operated with and without recycle. From the initial 430 g VSS (10 L at 43 g VSS/L) of biomass, the overall amount of biomass increased steadily through both ABRs more or less evenly through the compartments. Without recycle the final amount of active biomass in the reactor was of 756 g VSS. With recycle, the final biomass inventory was of 983 g VSS. Hydraulic effects in an ABR cause the biomass to be preferentially distributed within the upflow section of each compartment. This is advantageous since the partial fluidization of the biomass within the upflow sections increases the availability of the substrate to the granular biomass. Furthermore, as granules become entrained by affixed biogas bubbles, which made the biomass granules buoyant, a layer of floating biomass accumulated at the top of the upflow portion of each compartment as the biogas bubble would not disengage from the granule. As this layer of floating biomass grew with time, later granules displaced earlier granules, pushing the floating biomass layer above the level of the baffle tops. Biomass granules that were floating below the liquid level within the reactor, that is the biomass that was floating below the level of the baffle tops, were considered to remain active and in fact biogas

production within this floating layer was still evident. However, biomass that had been pushed above the level of the baffle tops was considered to be inactive, and as such, was ignored during calculations. Biomass above the level of the baffle tops was considered to have exited the reactor. Over time, this layer of inactive biomass served as a cap which prevented later biomass granules from rising up to the gas liquid interface and as such maintained later buoyant granules from exiting the compartment. This phenomenon served to increase the solids retention time of each compartment independently of the settling characteristics of the granular biomass.

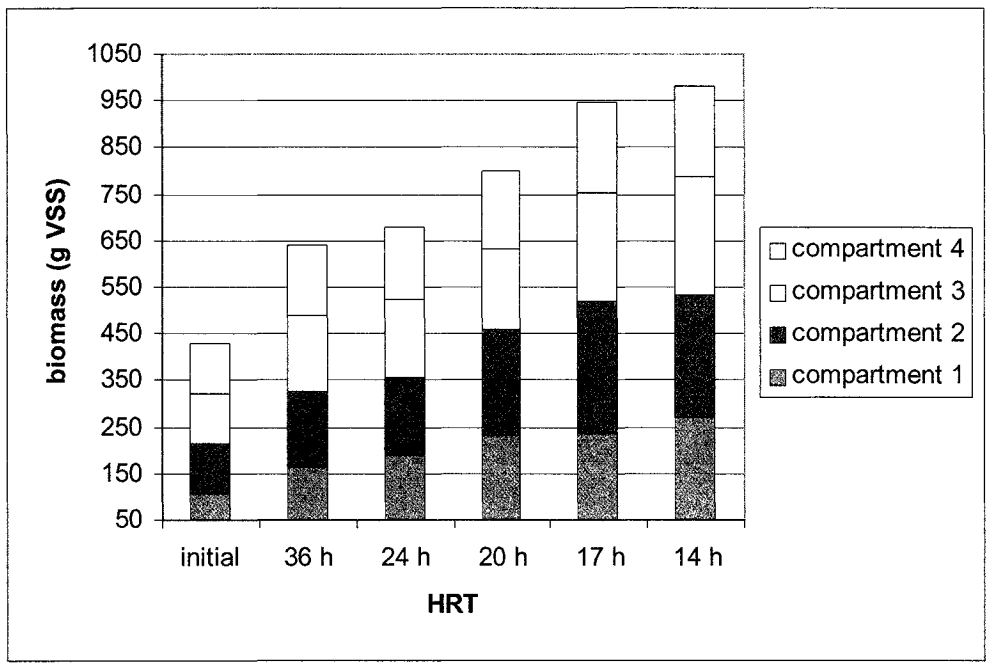

Figure 4.20: Biomass inventory across the reactor with recycle

4.2.6 Biomass Characteristics:

In conventional high rate reactors such as UASB reactors, the maximum rate at which the reactor can be run is limited by the settling characteristics of the granular biomass used therein. As such, the settling characteristics of the biomass used within high rate reactors are of particular interest. The granular biomass was tested using the conventional settling tests outlined previously. Three initial biomass samples, as well as biomass samples from each of the compartments of each reactor at the end of the experimental period, were tested. Settling curves were then generated for each of these

tests. Settling curves provide a qualitative comparison of the settling characteristics of each biomass sample, by studying the amount of biomass washed out at each of the successive upflow velocities. Generally, to facilitate comparison of different biomass samples, the settling velocity for the granular biomass, υ_{50}, is considered to be the velocity at which 50 % of the biomass has washed out.

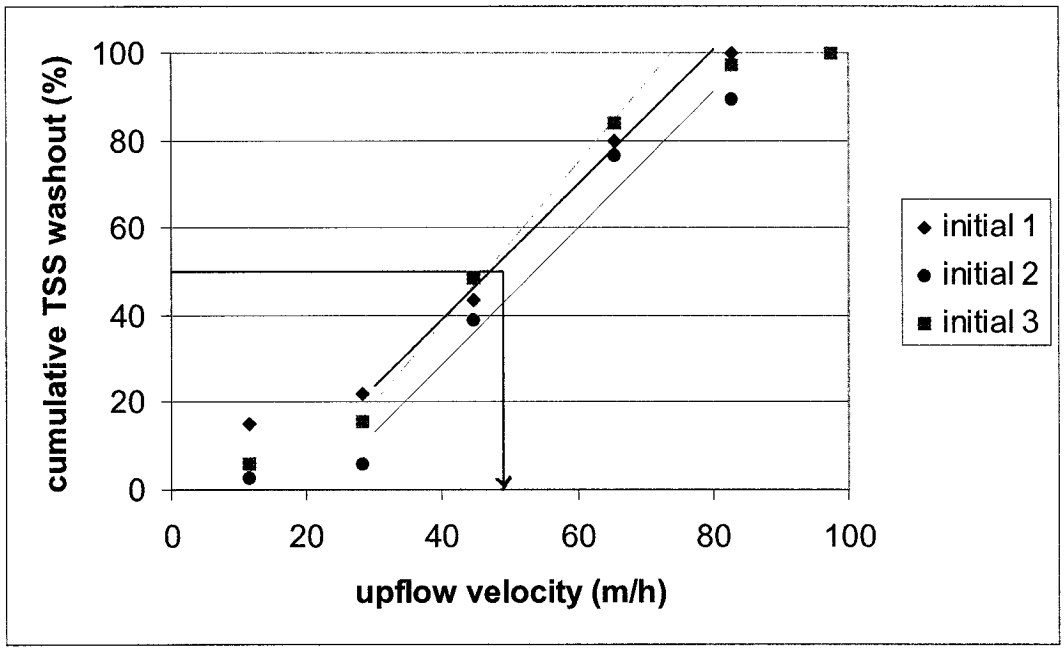

Figure 4.21: Settling test results for the seed biomass

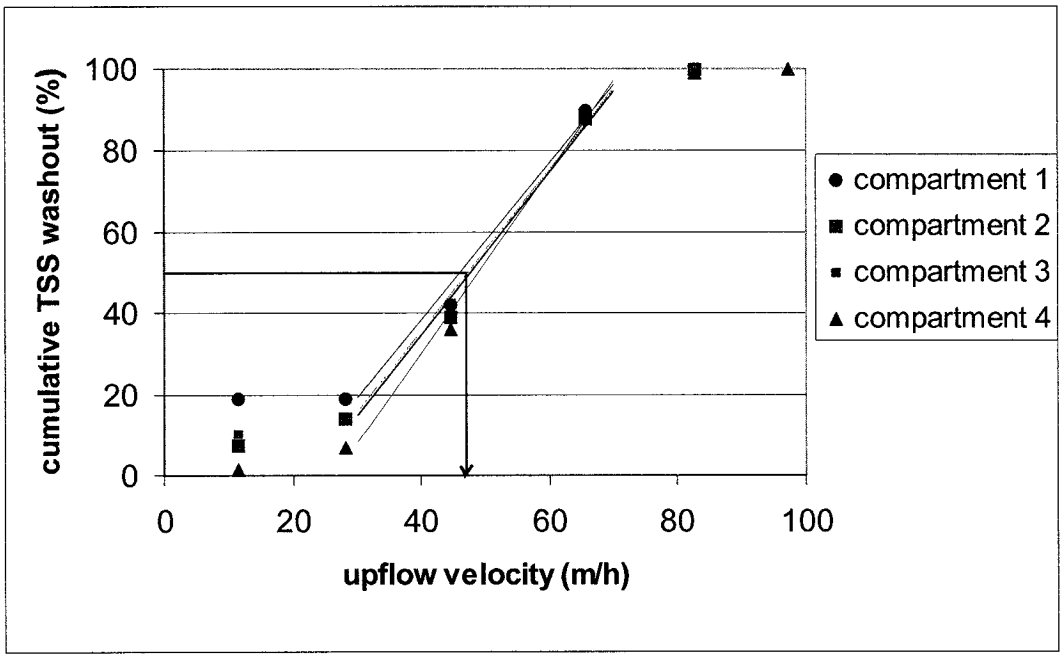

Figure 4.22: Settling test results without recycle at the end of the experimental period

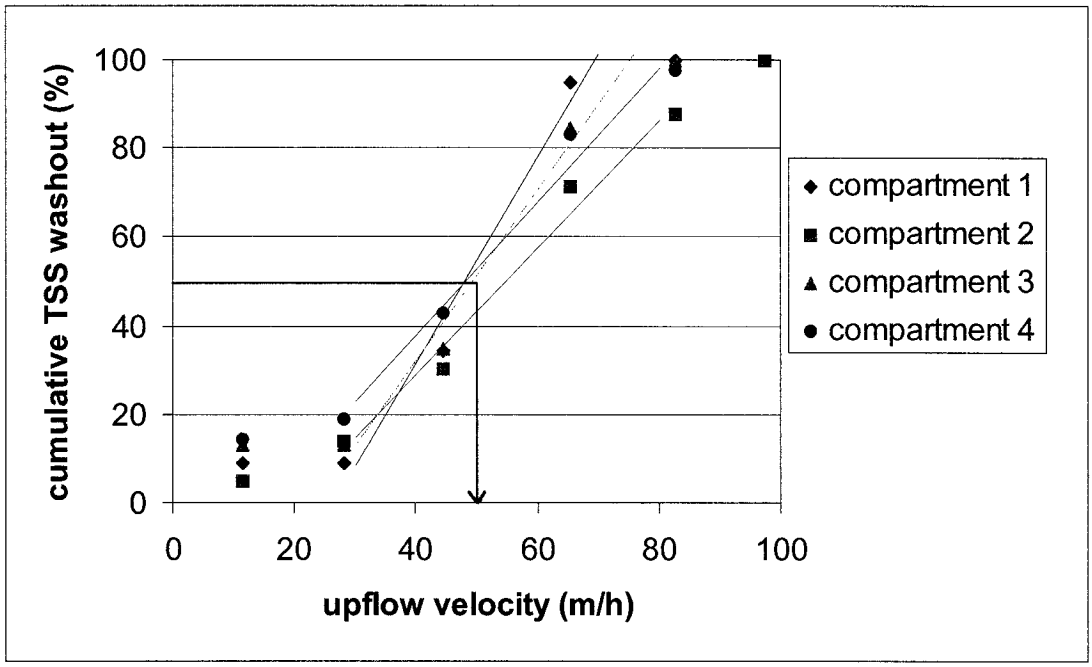

Figure 4.23: Settling test results with recycle at the end of the experimental period

The average υ_{50} for the initial biomass was of 49 ± 7 m/h. The biomass at the end of the experimental period for each compartment of the ABR with and without recycle, were found to have υ_{50} of 50 ± 5 m/h and, 47 ± 1 m/h respectively. In effect, no significant change in settling velocity was noted and all variations within the settling tests were well within the error associated with the test.

Contrary to the evolutionary settling characteristics for UASB reactors found by Pham (2002), the settling characteristics of the biomass within the ABR with and without recycle remained constant throughout the experimental period. and therefore the settling characteristics can not be correlated to the rate of washout of biomass.

As there was no significant change in the biomass's excellent settleability, there was also no change in the quality of the biomass. The biomass quality was found to have remained constant throughout experimental period. As shown in table 4.2, the volatile solids density within the granular biomass remained constant at 0.043 g VSS/mL while the fraction of volatile to total solids remained constant at 0.74 g VSS/g TSS. The only appreciable change in the quality of the biomass was that whereas the biomass was originally of a uniform black colour, with time the colouration of the biomass lightened

to a lighter brown (see figure 4.24). This phenomenon was first noted in the first compartment of the ABR operated with recycle and gradually spread through the ABR from first to the second compartment. This phenomenon was also observed by Hutňan et al.(1999) who attributed it to a shift within the granule to a predomination of acidogenic and hydrolytic bacteria. A predominance of acidogenic bacteria would agree with the compartmental VFA profiles which show a rapid conversion of the substrate ADF to acetic acid in compartments 1 and 2 (Figures 4.11-4.13 and 4.15-4.17).

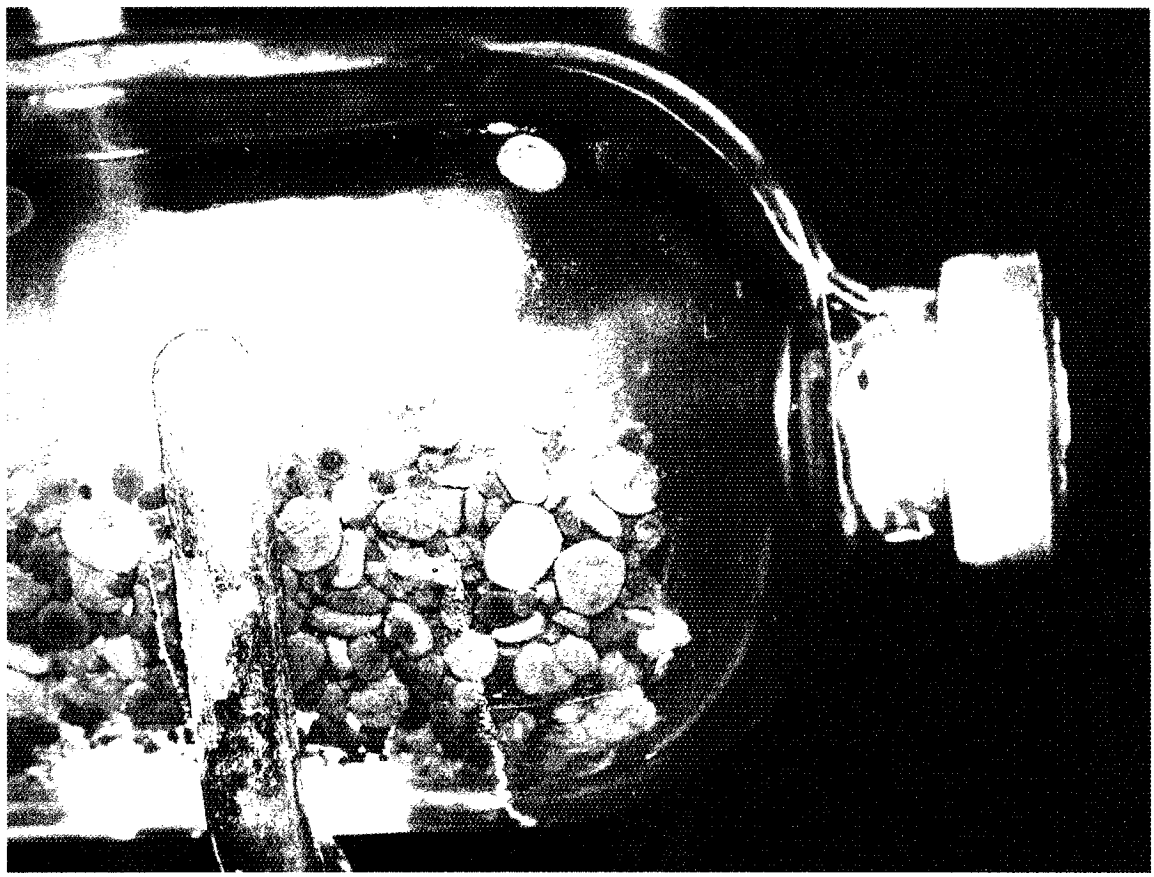

Figure 4.24: Biomass sample taken from compartment 2 of ABR operated without recycle at the end of the run period

Table 4.2: Biomass quality

units	value	standard deviation
g VSS/mL	0.043	3×10^{-5}
g VSS/g TSS	0.74	0.002

As mentioned previously, the amount of biomass in the ABR increased steadily with time. In the past, UASB reactors treating ADF at high OLR have had success which was limited by the loss of biomass due to washout. Reactors may successfully treat waste regardless of biomass washout provided that the rate of biomass growth and accumulation within the reactor is greater or equal to the rate of biomass loss. For this reason, it is important to quantify the yield of the biomass.

In the ABR without recycle, the overall biomass yield was found to be of 0.015 g VSS/g COD_{rem} while the overall yield for the ABR operated with recycle was found to be of 0.022 g VSS/g COD_{rem}. The greater overall yield noted in the ABR operated with recycle may be attributed to lower levels of stress within the reactor due to lower VFA concentrations. In previous tests with similar anaerobic granules treating 1.2 % ADF (COD = 8400 mg/L) the yield was found to be of 0.027 g/g COD removed and Speece (1996) lists the yield for mesophilic anaerobic bacteria treating similar wastes to be in the range of 0.01 to 0.054 g VSS/g COD and therefore the yield found in the ABR agrees well with previous results.

More important than overall yield is the net accumulated yield of biomass. A large biomass yield with a negative accumulation of biomass in the reactor would lead to reactor failure. The net accumulated yield within the ABR was found to be of 0.007 g VSS/g COD_{rem} when the ABR was operated without recycle and of 0.016 g VSS/g COD_{rem} for the ABR operated with recycle. In this case the ABR operated without recycle maintained 50 % of the biomass yield whereas the ABR operated with recycle maintained 70 % of the biomass yield. Both reactors showed good accumulation of biomass.

Although the settling characteristics were found to remain constant through the run period and to be the same in both the ABR operated with and without recycle, the amount of biomass washed out from the reactor with recycle was less than the amount of biomass washed out from the reactor without recycle. This is contrary to expectations since the ABR without recycle was run not only at a longer HRT, but did not suffer from the increased hydraulic effects experienced due to recycle. The biomass losses were not consistent throughout the run period, but the majority of losses occurred within short periods, or shock events. The greater amount of biomass retained within the ABR

operated with recycle may be attributed to better mixing. The increased mixing within the ABR operated with recycle may have served to promote detachment of gas bubbles from the anaerobic granules, thereby preventing accumulation of gases within the biomass bed and subsequently reducing the amount of shocks due to sudden release of biogases which would entrain losses of biomass.

It should be noted that although these yields are well within established ranges for mesophilic anaerobic yields, they are also very low. Although this is good for sludge management, any upset within the ABR that resulted in biomass washout would require a great deal of time to recover from biomass losses.

As mentioned previously, for UASB reactors treating ADF the SRT has proven to be the limiting factor in treatment rates. In ABR treatment of ADF however this was not the case.

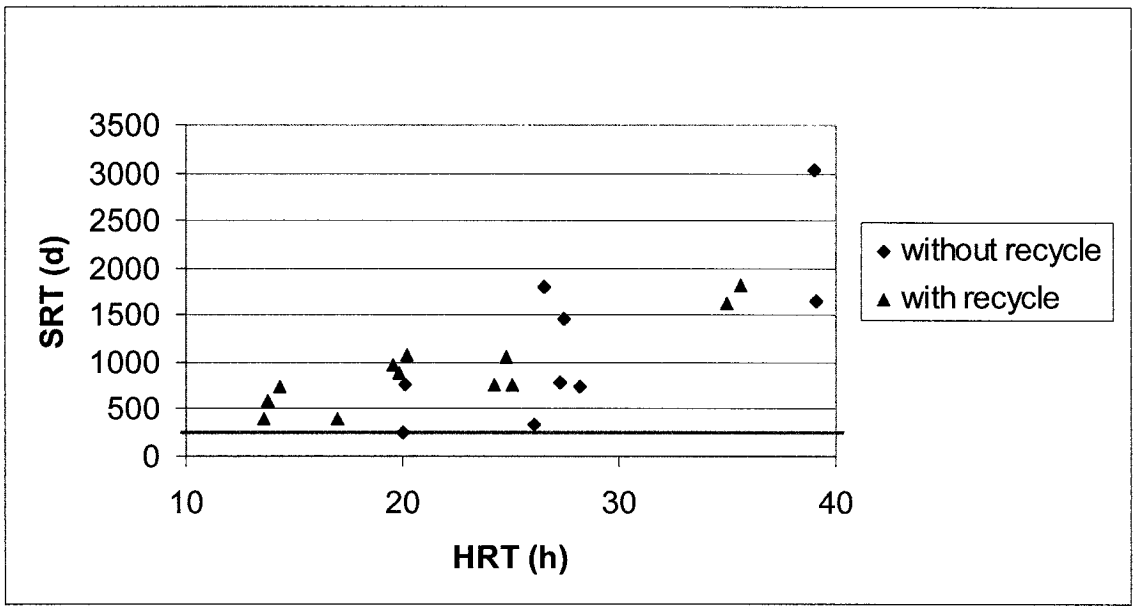

Figure 4.25: SRT variation with HRT, with and without recycle

The SRTs found for ABR treatment of ADF, as shown in Figure 4.25 remained above 250 d for all HRTs even after COD removal efficiencies had dropped below the 70 % acceptability limit (minimum of 260 d for 20 h HRT without recycle and a minimum of 400 d for 14 h HRT with recycle.) The horizontal line in Figure 4.25 represents the an SRT of 250 d, that is an SRT 10 to 15 times what is generally used in conventional anaerobic treatment systems. It should also be noted that SRT does not take into account

biomass growth and if growth were taken into account the SRT values would be infinite as is evident from biomass accumulation within the ABRs both with and without recycle. Therefore, as opposed to UASB treatment, where biomass losses have proven problematic, it is evident that in ABR treating ADF at HRT ranging between 39 h and 20 h without recycle and between 36 h and 14 h with recycle, the success of treatment is independent of SRT and in fact a method of biomass wastage would become necessary if a constant biomass concentration within the ABR were desired. The long SRT and positive biomass accumulation characteristics of ABR suggests successful application to shorter HRT and more dilute ADF is possible.

4.2.7 Acetoclastic Activity Tests:

AAT tests are generally used in order to determine the activity of a given biomass. A biomass sample is taken from the reactor and placed into serum bottles with a known amount of anaerobic medium. The bottle contents are first allowed to acclimate until the concentrations of VFA within the bottle drop to insignificant levels and then the bottles are injected with acetic acid feed stock. By monitoring the decrease in concentration of acetic acid with time it is possible to determine the acetoclastic activity of the biomass. Since the consumption of acetic acid can be correlated to methane production, and therefore to the reduction of COD in the system, it can be used to assess the effectiveness of a treatment system. Unfortunately, in this study, it was found that the batch tests did not accurately represent the continuous system within the reactor (see Appendix C).

Within the reactor, in any given compartment, VFA concentrations will remain fairly constant within one given steady state. In fact, this is why the stability of VFA concentrations can be used to determine whether or not the system is at steady state and why VFA concentrations are used to monitor anaerobic systems. Imbalances in the system will be heralded by changes in the VFA concentrations. In bottles however, the concentrations of VFAs drop with time as the biomass consumes the VFA. As such, the substrate concentration driving force decreases with time, thereby decreasing the rate of consumption of VFAs. Furthermore, some biomass samples have been acclimated to concentrations of VFA in their broad spectrum. As such biomass that has been within a

reactor compartment where the concentrations of longer chained fatty acids are higher will have a greater number of bacteria which are capable of degrading the longer chained acids and fewer bacteria capable of degrading acetic acid. In the case of biomass from the ABR with recycle, the biomass will have become acclimated to a different mixture of acids due to the biomass in the whole reactor and not only the biomass within that particular compartment or the preceding compartments. The variation of VFA concentrations as well as the type of VFAs from the reactor compartment to the acetoclastic activity serum bottle would adversely affect the microbial consortium thereby causing upset and an activity level which would not be representative of the activity within the ABR.

4.3 ABR Modeling:

4.3.1 Black Box Model:

The simplest model which can be applied to a reactor is the first order black box model, which is a model that ignores the concentration gradient within the reactor, taking into account the inlet and outlet concentrations only and establishes a substrate utilization rate constant, k^*, for the reactor as a whole. The k^* is said to be the superficial k since it does not account for dilution due to recycle and is only concerned with inlet and outlet concentrations. If equation 2 is to be applied to a reactor assuming CSTR conditions (concentration within the reactor is equal to the concentration at the outlet of the reactor) at steady state, it reduces to:

$$Q(S_0 - S_4) = kS_4XV \qquad \text{Eqn. 22}$$

or,

$$k^* = \frac{Q(S_0 - S_4)}{S_4XV} \qquad \text{Eqn. 23}$$

and since HRT = V/Q, equation 23 becomes,

$$k^* = \frac{1}{HRT \cdot X} \cdot \frac{S_0 - S_4}{S_4} \qquad \text{Eqn. 24}$$

where:

	k^*	=	superficial first order reaction rate coefficient (L/gVSS.d)
	HRT	=	hydraulic retention time (d)
	S_0	=	influent COD (g/L)
	S_4	=	effluent COD (g/L)
and,	X	=	average granular biomass concentration in the reactor (g VSS/L).

When equations 24 was applied to each HRT of each reactor the results for k^* presented in tables 4.3 and 4.4 were obtained.

Table 4.3: Black box first order reaction rate coefficients for ABR without recycle

HRT	39 h	27 h	20 h
k* (L/gVSS·d)	2.1	0.31	0.048

Table 4.4: Black box first order reaction rate coefficients for ABR with recycle

HRT	36 h	24 h	20 h	17 h	14 h
k* (L/gVSS·d)	1.4	2.9	0.94	0.59	0.10

As can be seen from tables 4.3 and 4.4 the black box or superficial first order reaction rate coefficient, k^*, varies greatly with HRT and with the presence or absence of recycle. There is a twenty-fold increase in the removal rate coefficient at 20 h when a 6:1 recycle ratio is present compared to the removal rate without recycle. In the ABR without recycle, the k^* is seen to decrease nearly 50-fold from an HRT of 39 h to and HRT of 20 h, and in the ABR with recycle the superficial k is seen to initially double from 1.4 to 2.9 L/gVSS·d as the HRT shortens from 36 h to 24 h then drop to 0.94 to 0.59 and finally to 0.10 L/gVSS·d as the HRT is shortened to 20 h, 17 h and 14 h respectively. From 24 h to 14 h the k^* dropped by more than an order of magnitude.

It should be noted that since black box modeling assumes that the concentration within the entire reactor is equal to the concentration of the effluent, it underestimates the substrate concentration driving force, and as such would have a tendency to overestimate the value of the first order reaction rate coefficient. Furthermore, this model does not account for the dilution effect of the recycle on the concentration into the first compartment, and as such for the ABR with recycle there a conflicting effect on the substrate concentration in the compartments since the recycle causes a dilution of the influent, yet the black box model assumes that the concentration throughout is that of the

effluent. Therefore, this model should show better results for the ABR with recycle than for the ABR without recycle, but neither could be used to predict ABR performance.

The model that was evaluated by Xing et al. (1991) was designed to overcome the limitations of the black box model. The Xing et al. (1991) model attempted to account for the substrate concentration driving force within each individual compartment including the dilution effect of the recycle.

4.3.2 The Xing et al. (1991) Model:

4.3.2.1 First Order Reaction Rate Coefficients

In their 1991 paper, Xing et al. presented a model to represent the performance of a HABR treating molasses wastewater. Although they state "The model parameters were determined by the least square method based upon experimental data," it is unclear how these calculations were performed although it is apparent that COD concentrations were used to represent the substrate concentration. In this present study, equations 9 through 13 presented on page 27, and the measured values of COD concentrations in each compartment, the amount of biomass in each compartment and the known values of Q and R were used to determine parameters k_1 to k_4 for ABRs running with and without recycle. The resulting first order reaction rate coefficients for each compartment can be seen in figures 4.26 and 4.27.

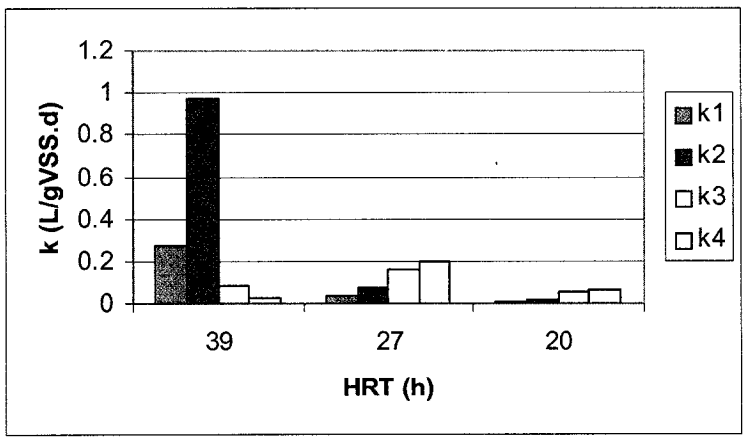

Figure 4.26: Xing model k coefficients without recycle

In the ABR operated without recycle (Fig. 4.26), the k coefficients rose from the first to the fourth compartment. For example, at a HRT of 27 h the k coefficient rose

from 0.039 L/g VSS·d in compartment 1 to 0.078, 0.16 and 0.20 L/g VSS·d in compartments 2, 3 and 4 respectively. However, at a HRT of 39 h the k coefficient initially rose from 0.28 to 0.98 L/g VSS·d from compartment 1 to compartment 2, then decreased to 0.086 and 0.026 L/g VSS·d in compartments 3 and 4 respectively. Since the first order reaction rate coefficient is an indication of COD removal, it is therefore an indication of methane production. The k coefficients in the ABR without recycle indicate that methanogenesis occurred first within the first compartment and then rose sharply in the second compartment, the fall of methane production in the third compartment indicates that the last two compartments were substrate concentration limited. That is, the first two compartments consumed the majority of the substrate and as such the last two compartments were operating in starvation conditions. The overall decrease in k coefficients from an average of 0.3 L/g VSS·d at 39 h to 0.1 L/g VSS·d at 27 h and to 0.04 L/g VSS·d at 20 h HRTs is indicative of the overall decrease in efficiency with the concomitant increase in VFA concentrations, especially the longer chained VFAs in all compartments thereby inhibiting methanogenesis.

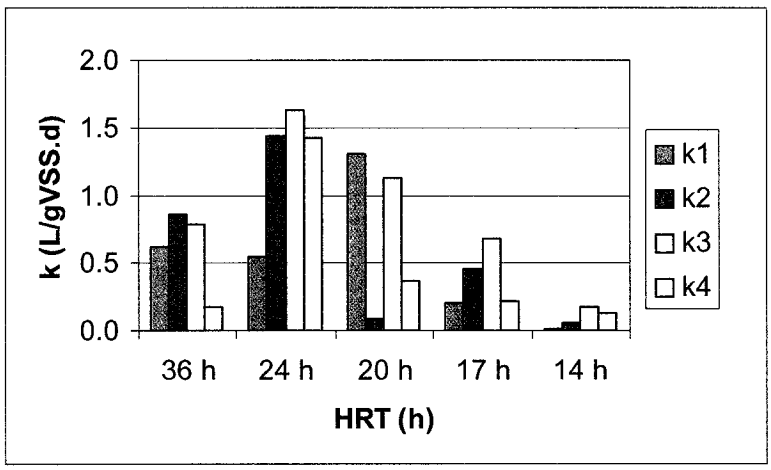

Figure 4.27: Xing model k coefficients with recycle

In the ABR operated with recycle (Fig. 4.27), the k coefficients rose from the first compartment to the second or third compartment before falling in the final compartment. For example, at a 24 h HRT the k coefficients rose from 0.55 L/g VSS·d in the first compartment to 1.4 and 1.6 L/g VSS·d in the second and third compartments respectively and then fell back to 1.4 L/g VSS·d in the fourth compartment. As was seen in the case

of the ABR operated without recycle an HRT of 39 h (Fig. 4.26), these profiles seem to indicate that the majority of methanogenesis (waste stabilization) occurred first within the first compartment and continued to occur in the second compartment and third compartments. The decrease in methanogenesis in the fourth compartment indicates that the final compartment may have been substrate concentration limited. In other words, in the final compartment the anaerobic microbial consortia were operating in starvation conditions with a high potential for substrate consumption with little substrate to consume.

Unlike the ABR operated without recycle, the ABR operated with recycle experienced an overall increase in k coefficients with shortening HRT from 36 h to 24 h before experiencing a decrease in k coefficients at HRTs of 24 h to 20 h to 17 h and finally to 14 h. For example, the average k coefficient at 36 h HRT was 0.6 L/g VSS·d while at 24 h, 20 h, 17 h and 14 h HRTs the average k coefficients were of 1 L/g VSS·d, 0.7 L/g VSS·d, 0.4 L/g VSS·d and 0.1 L/g VSS·d respectively.

4.3.2.2 Difficulties with First Order Reaction Rate Coefficients

As previously mentioned, Xing et al. (1991) used COD to represent the substrate concentration in their work and as such, k should have been presented with units of (g COD removed/g COD_{in})/(g VSS·d /$L_{influent}$) and not with units of d^{-1}. It is also noted that one of the assumptions made by Xing et al. (1991) was that methanogenesis of acetic acid was considered to be the rate limiting step in anaerobic digestion and that the kinetic coefficients used in the Xing et al. (1991) study were therefore based on first order reaction of acetic acid. Unfortunately, the use of COD as the measure of the substrate concentration does not hold with the assumption that the k coefficients are substrate utilisation rates based on methanogenesis of acetic acid. While it is true that the substrate concentration driving force for methanogenesis would indeed be the concentration of acetic acid within the compartment, a COD measurement cannot be said to be representative of the acetic acid concentration in all compartments and the consumption of acetic acid itself may not be first order. If the acetic acid concentration were used instead of the COD to represent the substrate concentration however, k could no longer be said to be a first order reaction rate coefficient as acetic acid is not only consumed but

is also produced within the ABR. In the feed used by Xing et al. (1991) for example the COD was due not only to the concentration of acetic acid therein, but also to the proteins and other components found therein which, through the action of the hydrolytic and acidogenic microbial florae were broken down thereby creating acetic acid which increase the substrate concentration driving force. In the present study for example, k_1 would be incalculable for a reactor without recycle since there is no acetic acid in the feed, thereby producing the result that $k_1 = -Q_1/W_1$. Since the COD decrease through the first compartment makes it obvious that this was not in fact the case and that methanogenesis did occur within this compartment, then the assumptions made by Xing et al. obviously render the k coefficient calculated thereby unusable as a basis of comparison. Since acetic acid is both created and consumed in anaerobic digestion and since high acetic acid concentration simultaneously inhibits and promotes methanogenesis, the assumption that the overall reaction rate is first order with acetic acid concentration does not hold and since the coefficients calculated using the Xing et al. (1991) model can not account for this phenomenon, nor for substrate-limited conditions, no predictive correlation of k with HRT or OLR can be achieved.

4.3.2.3 Specific Substrate Utilization Rate

In order to find a more appropriate basis of comparison for different systems, it was necessary to multiply k by its corresponding substrate concentration (as COD), which in effect yields the specific substrate utilization rate (U) with units of g COD removed/g VSS·d. Since U is based upon the COD consumption within the reactor, it is therefore based upon the methanogenesis which occurs therein and is thereby an appropriate indicator of the consumption rate within the ABR.

The specific substrate utilization rate (U) with units of g COD removed/g VSS·d, may be determined from the SOLR using the following equation:

$$U = SOLR \times \frac{(COD_{in} - COD_{out})}{COD_{in}} \qquad \text{Eqn. 25}$$

In order to determine the overall U through the entire reactor, COD_{out} is the COD exiting the reactor and COD_{in} is the COD of the feed. When determining the compartmental

COD, the COD_{in} and COD_{out} are the COD in and out of the compartment respectively (Eqn. 25).

Since U is a measure of the consumption of COD and since COD consumption occurs through methanogenesis and further the methanogens consume acetic acid, substrate concentration driving force is accounted for when utilizing U as a descriptor of reactor performance and a basis of comparison for different systems. A high acetic acid concentration increases the substrate concentration driving force and thereby U. The conflicting effect of high VFA concentrations, that is the conflict between the inhibitory effect of VFAs and the substrate concentration driving force increase associated with an increase of acetic acid, makes it difficult to predict ABR treatment at varying HRT. It isn't clear to what extent acetic acid itself is inhibitory provided that a neutral pH is maintained. Acetic acid may only be inhibitory to the extent that high acetic acid concentrations may inhibit acetogenesis, that is production of acetic acid from longer chained volatile fatty acids such as butyric and propionic acids. Inhibition of acetogenesis would decrease the production of acetic acid and thereby the substrate concentration driving force while increasing the amount of these longer chained fatty acids which would pass untreated through the system thereby increasing effluent COD and decreasing the overall efficiency of the ABR.

The specific substrate utilization rate is a function of the specific organic loading rate (SOLR). Just as the OLR is a measure of the amount of COD fed to the reactor per unit volume of reactor and unit time, the SOLR is a measure of the amount of COD fed to the biomass within the reactor per unit mass of active biomass per unit time . It is possible to define OLR and SOLR on a compartmental level as well, where the SOLR of the first compartment is a function of the influent concentration and the mass of biomass contained within that compartment. Just as with OLR, the strength of the waste exiting the first compartment will determine the SOLR of the following compartment since the effluent of the first compartment is the influent of the second. However, unlike the OLR where, without recycle, the overall OLR is a fraction of the first compartment's OLR (in this case, it is ¼ of the first compartment OLR since the reactor is divided into 4 equally sized compartments), the overall SOLR will not necessarily be directly correlated to the

first compartment SOLR since the amount of biomass per compartment varies from compartment to compartment as well as over time.

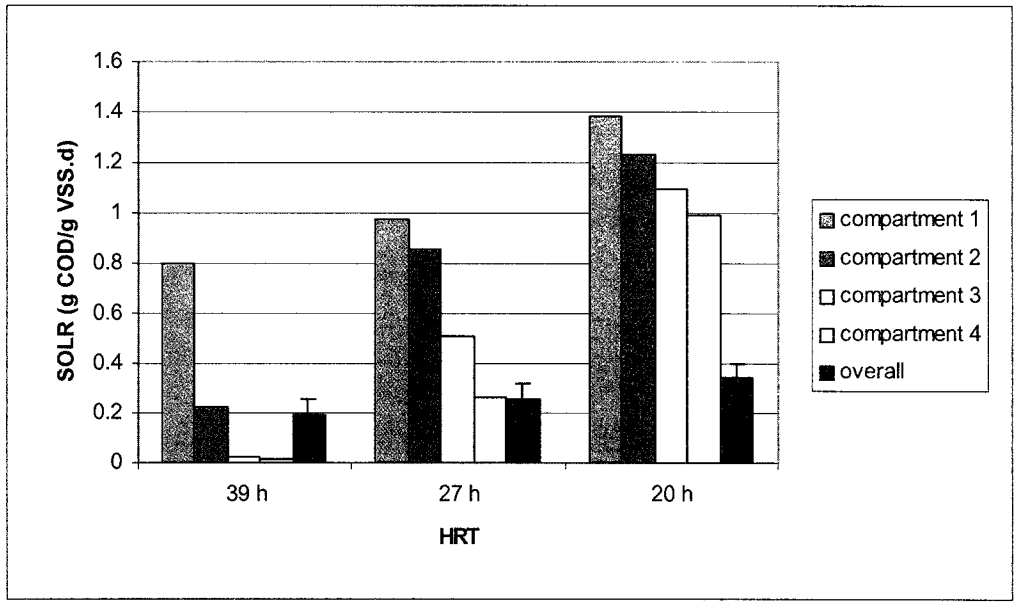

Figure 4.28: Specific organic loading rate profiles, without recycle

As can be seen from Figure 4.28, the SOLR of the first compartment was the greatest with each subsequent compartment having a lower SOLR as substrate was consumed within the ABR. For example, at an HRT of 27 h the SOLR within compartment 1 was of 0.97 g COD/g VSS·d while the SOLRs of compartments 2 through 4 were of 0.86, 0.51 and 0.26 g COD/g VSS·d respectively. The SOLR also rose with shortening HRT, as the feed rate increased, and as such the amount of substrate fed to the reactor per unit time increased. For example within the first compartment the SOLR was of 0.80 g COD/g VSS·d at a 39 h HRT, 0.97 g COD/g VSS·d at a 27 h HRT and 1.4 g COD/g VSS·d at a 20 h HRT.

As can be seen in Figure 4.29, the overall specific substrate utilization rate varied insignificantly (values 0.19, 0.23, 0.17 g COD_{rem}/g VSS·d where the error bars show ± 2 standard deviations), while the compartmental Us varied significantly. This figure shows how variation of compartment number and size could affect the overall treatment efficiency. The U is an appropriate indicator of reactor performance in that it is independent of biomass concentration within the reactor or substrate concentration,

however, U is still subject to variations due to extremes of substrate or VFA concentrations. As was shown at the 39 h HRT for the ABR operated without recycle (Figure 4.28), low substrate concentration (concentrations less than about 100 mg/L), such as those in the last two compartments, lead to a lower U as the microbial consortia had to compete for dwindling resources. As the compartmental COD concentrations dropped from 2000 mg/L in compartment 1, which exhibited a U of 0.56 g $COD_{removed}$/g VSS·d, to 200 mg/L in compartment 2 the U value decreased by 64 % and when the compartmental COD concentration dropped to 100 mg/L in compartments 3 and 4 the U value dropped by an order of magnitude.

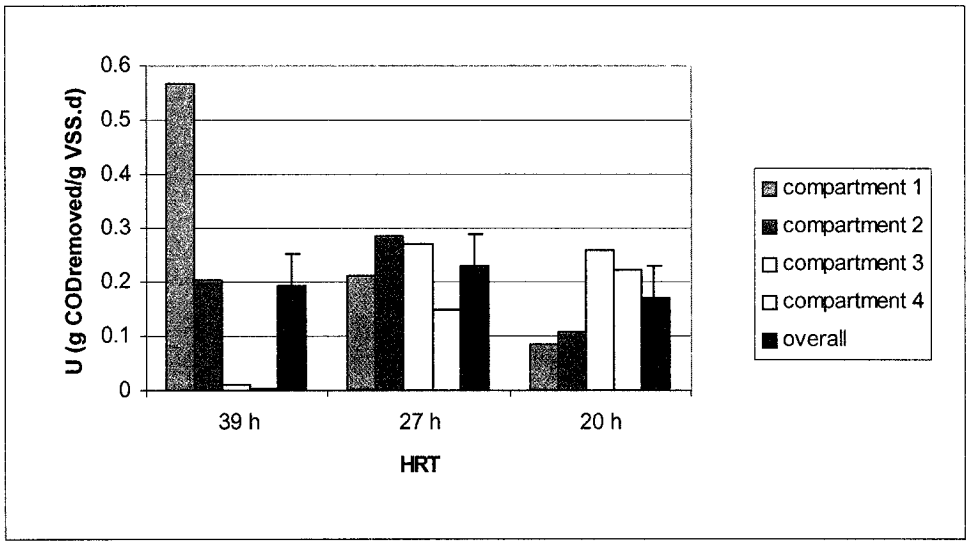

Figure 4.29: Specific substrate utilization rate profiles, without recycle

As the VFA concentrations increased in the early reactor compartments with shortening HRT, the U values decreased accordingly since U is an indication of methanogenesis (consumption of COD and therefore VFA) and increased VFAs are an indicator of increased acidogenesis. For example, as the HRT shortened from 27 h to 20 h (Fig. 4.27), the U in compartments 1 and 2 were reduced by half as acidogenesis predominated therein. The last two compartments however maintained higher U values as the VFAs were consumed through methanogenesis and the VFA concentrations decreased.

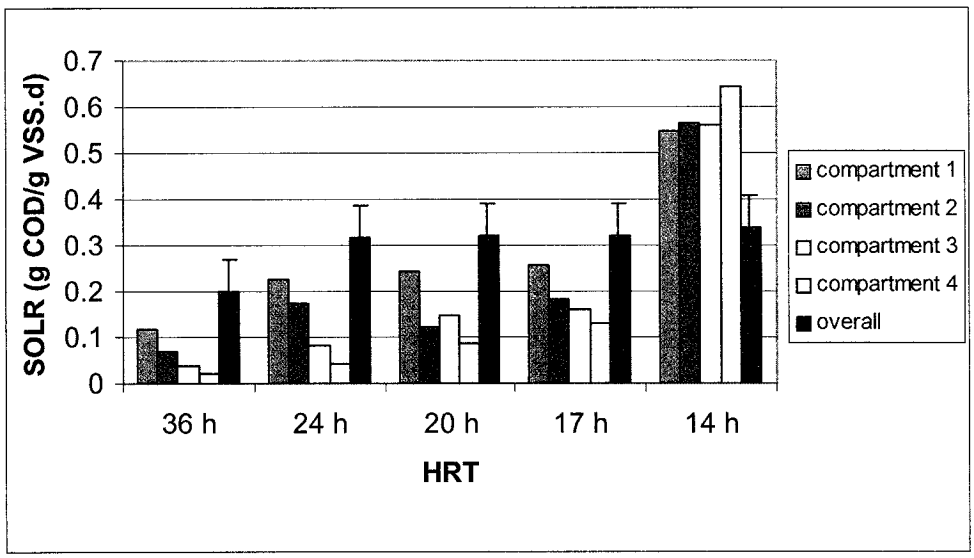

Figure 4.30: Specific organic loading rate profiles, with recycle

Figure 4.30 demonstrates the effect of recycle on SOLR at the compartmental level. Although overall SOLR for the ABR operated with recycle was on the same order as the SOLR for the reactor operated without recycle, due to the dilution effect of the relatively dilute effluent being mixed with the influent the loading rate to the first compartment was proportionately lower than that without recycle. In the case of the 14 h HRT however, the effluent concentration remained high and as such the influent concentration rose accordingly thus accounting for the dramatic increase in compartmental SOLR at that HRT. It should be noted that although the OLR increased between HRT of 24 h and 14 h, the SOLR did not increase significantly due to the growth of biomass during the intervening period.

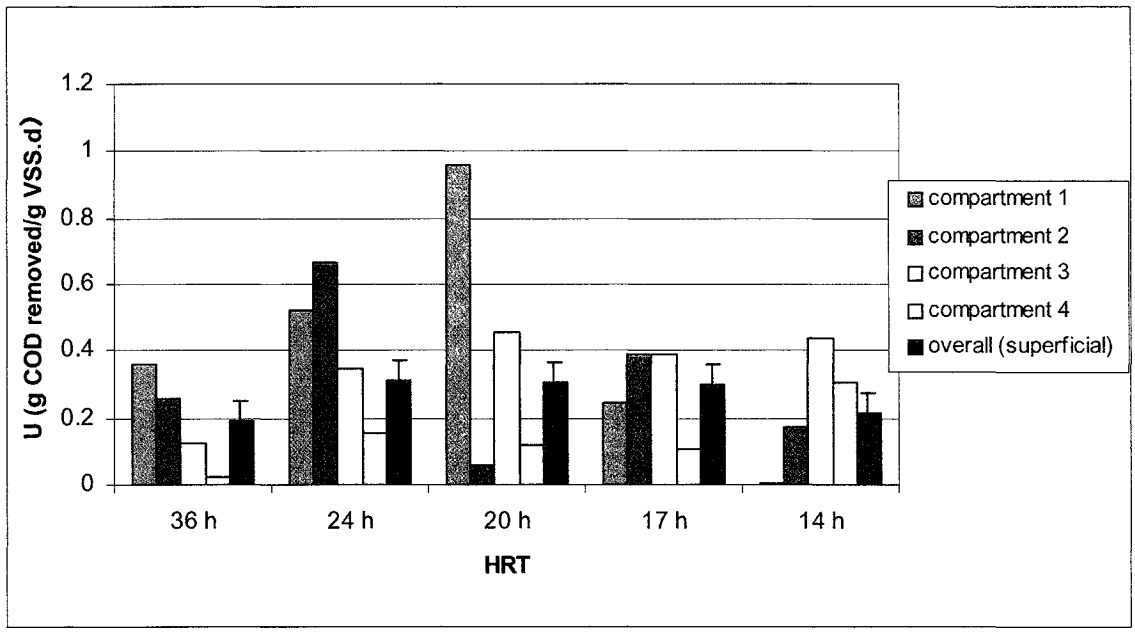

Figure 4.31: Specific substrate utilization rate profiles, with recycle

The specific organic removal rates within the reactor with recycle, as seen in figure 4.31 show the same type of trend with values of the same magnitude as those without recycle.

As can be seen in Figure 4.31, although the overall specific organic removal rate did not vary significantly (values, 0.19, 0.31, 0.31, 0.30, 0.22 g/g·d), the compartmental removals varied significantly. Unlike the ABR without recycle (Fig. 4.29), in the reactor with recycle (Fig. 4.31) U actually increased with shortening HRT due to increasing OLR and therefore increasing substrate concentration driving force, up to a limit between the 24 h and 20 h HRT, when it decreased again. As previously mentioned, due to growth of biomass, although the OLR increased between HRT of 24 h and 14 h, the SOLR did not increase significantly and therefore the increase in U due to the substrate concentration driving force was attenuated by the decrease in U due to the increase in the amount of biomass within the reactor. At the 17 h HRT, it is evident that VFA concentrations had become inhibitory and HRT too short thereby leading to a decrease in the value of U for HRT shorter than 17 h. As was the case with the ABR operated without recycle, the decrease in U at low substrate concentrations was again visible for the ABR operated with recycle.

As the HRT shortened, and the outlet acid concentrations increased (with the concurrent COD increase) the amount of acids returned to the inlet via the recycle increased. Therefore the increased acid concentration in the first compartment may have been due to returning acid from the last compartment and not due to an increase in acidogenic activity. At an HRT of 14 h, no appreciable U was seen in the first compartment with methanogenesis occurring in compartments 3 and 4.

4.3.2.4 Modeling Based Upon Specific Substrate Utilization Rate

Although U is a more appropriate descriptor of reactor performance than k and thereby a better basis of comparison for different systems, it should be noted however, that a model based on U would not be useful for predicting the COD out of the reactor or the intermediate COD concentrations. Firstly, since U is dependent on the COD concentration in the compartment, and in CSTRs the concentration in the reactor is the concentration out of the reactor, the outlet concentration is required in order to calculate U. Since U is a measure of the consumption of COD and since COD consumption occurs through methanogenesis and further, since methanogens consume VFAs the "substrate" consumed and therefore the "substrate concentration driving force" are due to the VFAs. A high acetic acid concentration therefore increases the substrate concentration driving force and thereby the U. The effect of substrate-limited conditions in some reactor compartments as well as the conflict between the inhibitory effect of high VFA concentrations and an increase in the substrate concentration driving force, make it difficult to model ABR treatment of ADF at varying HRT and the Xing et al. (1991) CSTR-in-series model can not account for these phenomena.

In the study conducted by Xing et al. (1991), their relatively small COD concentration range and low VFA concentrations through the reactor would account for the relatively constant k values they reported. If the COD concentration differential had been greater, or the VFA concentrations higher, a variation in the k coefficients with OLR would have been noticed and the use of an average k coefficient over a range of OLR would not have been appropriate. For the same reason, it would not be appropriate to use an averaged U or k coefficient value for each compartment over a range of OLR and therefore prediction of results over a range of HRT or correlation of averaged U or k

with HRT would not be possible. It may however, be possible to use an average U value for each OLR as long as the concentration gradient through the reactor were not too great and as long as the VFA concentrations were not inhibitory. For these cases, the variation in substrate concentration driving force and the inhibition due to the VFA concentrations may be reduced and U may be correlated with the HRT, and as such could be substituted into the overall equation (Eqn. 6) in order to predict the outlet concentration under these conditions. In the current study however, the inhibitory effects of VFA concentration combined with the rate decrease associated with the reduced substrate driving force in latter compartments made this impossible.

4.3.2.5 Effect of Recycle

It is evident from these results that data from an ABR operated without recycle could not be used to predict the effect of adding recycle in cases where the COD out of the final compartment remains negligible. When the COD concentration out of the final compartment is low, the dilution effect of recycle in ABR, reduces the substrate concentration driving force but also increases the mixing and therefore the mass transfer rate within the compartments thereby increasing the U for the same substrate concentration driving force. Further, since the inhibitory effects of the VFAs are delayed to shorter HRT, greater influent throughputs are possible at high removal efficiencies. As it is desirable to have the greatest throughput at the highest removal efficiency (COD out of final compartment remains low), for treatment of ADF in an ABR, recycle is preferable. As Levenspiel (1999) points out, in the case of CSTR in series with recycle and throughflow where the recycle is relatively rapid compared to the throughflow, the system as a whole acts as one large CSTR. As such, the theoretical number of CSTR in series differs greatly from the actual number of compartments. When this is the case, the assumptions in the model proposed by Xing are negated and the predictions for the reactor without recycle, which would have a greater number of theoretical CSTR in series, could not be applied. This theory however, does not appear to apply for cases where the concentration of the effluent from the final compartment remains low. CSTR-type profiles were not observed save for the 14 h HRT where the COD concentration out of the final compartment was high.

4.4 Evaluation of ADF Treatment Efficiency in ABR

The Albany Airport has achieved 95 % COD removal efficiency of propylene based ADF in a 700 L AFBR at an influent COD of 5000 mg/L, an HRT of 8 h and an OLR of 15 g COD/L·d and achieved 82 % COD removal efficiency at a 5 h HRT and an OLR of 25 g COD/L·d (Switzenbaum et al., 1999). The maximum OLR attained in the ABR of the current study with acceptable COD removal rates was for the ABR operated with a recycle ratio of 6:1 which achieved 93 % COD removal efficiency at an OLR of 9.9 g COD/L·d. Although the ABR was not able to achieve the same removal efficiency at the same volumetric loading rates as the AFBR it isn't clear how much biomass was utilized in the AFBR at the Albany Airport and it is therefore difficult to compare the actual substrate removal rates. Additionally, while fluidization increases mass transfer the costs of operation of the AFBR would be substantially more than for an ABR which has much lower pumping requirements.

Mulligan et al. (1997) successfully treated UCAR XL 54 ADF (the same ADF used in this present study) at similar influent COD (8,500 mg COD/L) in a 900 L anaerobic multiplate reactor operating at 39°C and 12 h HRT. Mulligan et al. (1997) were able to achieve 90 % COD removal efficiency at a SOLR of 0.79 g COD/g TSS·d, in other terms, Mulligan et al. achieved a U of 0.7 g COD_{rem}/g TSS·d at a biomass concentration of 21 g TSS/$L_{reactor}$ whereas this present study has achieved a U of 0.32 g COD_{rem}/g VSS·d at a biomass concentration of 31 g VSS/$L_{reactor}$. Since the VSS/TSS ratio was found to be of 0.74 g VSS/g TSS these results would become a U of 0.22 g COD_{rem}/g TSS·d at a biomass concentration of 42 g TSS/$L_{reactpr}$. In short, Mulligan et al. achieved more than three times the specific substrate utilization rate that was achieved in the ABR at similar conditions.

Nachaiyasit and Stuckey (1997b), while treating a sucrose/peptone waste with a concentration of 4,000 mg COD/L in an 8 compartment ABR found that it was necessary to chose between operating at a maximum SOLR or at a maximum U. They found that a maximum COD removal efficiency of 98 % could be achieved at a SOLR of 0.39 g COD/g VSS·d and a U of 0.38 g COD_{rem}/g VSS·d (similar results to those found in the present study), while a maximum U of 0.66 g COD_{rem}/g VSS·d could be achieved with a COD removal efficiency of 90 % at an SOLR of 0.73 g COD/g VSS·d and a maximum

SOLR of 0.78 g COD/g VSS·d could be achieved at a COD removal efficiency of 52 % and a U of 0.41 g COD_{rem}/g VSS·d. Similarly, Grobicki and Stuckey (1991) found that it was possible to achieve high U values (up to 1.1 g COD_{rem}/g VSS·d) at low biomass concentrations (3.5 g VSS/$L_{reactor}$) and at high SOLR (1.4 g COD/g VSS·d) but that this entailed a loss in overall efficiency. This indicates that a choice must be made between achieving high SOLR with it's consequent low COD removal efficiency and high COD_{out}, and achieving a high U with a high (although not the highest) COD removal efficiency. As concluded earlier, a high U value is indicative of good reactor performance and in the operation of ABRs, optimizing U may lead to the best overall treatment of ADF wastes.

When treating high strength molasses wastewater using granular biomass in an HABR, Boopathy and Tilche (1991) achieved similar results to those found in the present study. At a SOLR of 0.4 g COD/g VSS·d a COD removal efficiency of 82 % was achieved at a U of 0.33 g COD_{rem}/g VSS·d.

4.4.1 Effect of Biomass Granule Size Distribution

Nachaiyasit and Stuckey (1995) stated that an increase in substrate concentration driving force leads to an increase in specific microbial activity as HRT get shorter and concomitantly COD removal efficiencies remained constant as HRT varied from 40 h to 20 h. Grobicki and Stuckey (1991) noted however that above a particular SOLR (in their case, above a SOLR of 1.5 g COD/g VSS·d) the increase in the mass transfer rate due to an increase in substrate concentration driving force is too slow to allow the reaction rate to rise enough to maintain high efficiency at greater throughput. The authors also postulated that an increase in average diameter of the granular biomass as the flowrate increases due to the washout of smaller granules, may also lead to a decrease in efficiency. The growth of the biomass granules and increase in the granule diameter witnessed during the trial period of this present study could account for a decreased mass transfer efficiency and therefore the reduced COD removal efficiency seen at a 14 h HRT in the ABR with recycle. Although the overall settling characteristics of the biomass granules remained the same through the run period, the multitude of smaller granules which made up the fractions washed out at low upflow velocities in the seed biomass

were replaced, in the samples taken at the end of the run period, by fewer large granules having poor settling characteristics. Thus, although the settling profiles didn't change, the size distribution of the granules did. The variation of treatment efficiency with the size distribution of the biomass granules may prove an interesting subject for future studies. If the mass transfer through the granules becomes limiting due to an increased granule diameter, this could account for increased VFA concentrations, and thereby also account for the reduced treatment efficiencies witnessed at the end of the run period. It may be possible to achieve acceptable COD removal efficiencies of 1 % ADF feed at HRT less than 20 h without recycle and at HRT less than 14 h for ABR operated with recycle if the diameter of the biomass granules were smaller than those found at the end of the run period and as such further studies in this SOLR range are advisable while monitoring biomass granule size distribution. Alternately, granule size distribution would affect the expansion of the granule beds and perhaps modeling based on expanded beds in series would be appropriate.

4.4.2 Improved Mixing

If mass transfer rate becomes limiting at high SOLR, the effect would be compounded in parts of the ABR where acidification predominates and there is little gas evolution to improve mixing which replenishes the substrate supply near the biomass granules. This phenomenon, coupled with the increased granule size in the ABR at the end of the run period, could also explain why better treatment efficiency of ADF was achieved by Pham (2002) in UASB reactors. Pham (2002) treated UCAR XL 54 ADF in bench scale UASB reactors with a recycle ratio of 4:1 and achieved 98 % removal of 1 % ADF feed at a SOLR of 0.63 g COD/g VSS·d at a HRT of 12 h, that is a U of 0.62 g COD_{rem}/g VSS·d and a biomass concentration of 32 g VSS/$L_{reactor}$. At an identical biomass concentration, the maximum U achievable with acceptable removal efficiencies in the current study was of 0.35 g COD_{rem}/g VSS·d at a SOLR of 0.32 g COD/g VSS·d, a HRT of 17 h and a recycle ratio of 6:1. The columnar shape of the UASB reactor would promote mixing through the whole of the reactor volume, as the gas produced in the lower section of the reactor must rise through the entirety of the liquid column. The circular cross section of UASB reactors would also reduce the stagnation zones that are

naturally found in the corners of rectangular reactors and thereby the UASB reactors would make better use of the available biomass.

Grobicki and Stuckey (1992) found that although clean reactors had very little dead space (between 1 % and 8%) that RTD studies for working reactors showed up to 20 % dead space. The authors noted that at an HRT of 10 h channelling appeared to be significant, but that at an HRT of 5 h the increase in flowrate prevented channelling from occurring by maintaining the granular biomass beds in a fluidized state and thus decreasing the dead space. At low HRT they found that the presence of biomass did not significantly increase the volume of dead space in the ABRs.

The hydrodynamics of the ABR could possibly be improved by simply reducing the HRT to below a threshold value as proposed by Grobicki and Stuckey (1992) and it may be possible to treat ADF successfully in an ABR without recycle at HRT less than 20 h or in ABR with a recycle ratio of 6:1 at HRT less than 14 h if channelling were reduced through fluidization of the granular biomass beds at shorter HRT. Compartments which are overfull of biomass are difficult to fluidize and as such, biomass wasting may improve hydrodynamics. Alternatively, the hydrodynamics could be improved by reducing the width and increasing the height of the compartments while maintaining the same compartment volume thereby increasing the liquid column within each compartment as in the UASB reactors. This would, however, not increase the mixing within the compartments where acidification predominates. It may also be possible to increase mixing in the first compartment of the ABR through the addition of a feed box thereby spreading the influent liquid out more evenly over the influent end of the reactor. The addition of intra-compartmental recycle or inert gas bubbling (e.g. N_2) would also increase mixing and may bear further study.

4.4.3 Evaluation of Xing et al. (1991) Predictions:

Xing et al. (1991) predicted that in HABR operated without recycle at constant OLR the COD removal efficiency would increase with increasing substrate concentration, that (b) short HRT will lead to decreased COD removal efficiency and that (c) COD removal efficiency will increase with increasing biomass mass until a certain point is reached and that above this critical bacterial mass COD removal efficiency

becomes independent of bacterial mass and that (d) recycling reduces COD removal efficiency. The present study upholds the first two conclusions made by Xing et al. (1991) for ABR treating ADF. The first two conclusions (a and b) are in fact linked, an ABR treating ADF operated at a higher substrate concentration and a longer HRT would achieve higher COD removal efficiency than one operated at a lower substrate concentration at a shorter HRT at the same OLR, this is due both to an increased substrate concentration driving force and to an increase in the time available to the biomass for treatment. The conclusion (c) that COD removal efficiency may become independent of biomass mass above a critical bacterial mass holds true since it has been shown in the final two compartments at 39 h HRT in the ABR without recycle, that some biomass may become inactive due to excessively low substrate concentration driving force. Although the present study does not allow for direct confirmation of the conclusion that, at constant OLR, COD removal efficiency will increase with increasing biomass mass up to a critical bacterial mass above which COD removal efficiency becomes independent of bacterial mass, it is expected that increased biomass would increase COD removal efficiency for ABR treating ADF provided VFA toxicity and substrate concentration limitations were low. The final conclusion set forth by Xing et al. (1991), namely that recycling reduces COD removal efficiency, is not true in the case of ABR treating ADF. The mere presence of recycle does not, in fact, reduce COD removal efficiency in ABR treating ADF although it does reduce the substrate concentration driving force. This may be due to the toxic nature of the ADF feed, or to improved mixing due to higher throughflow. There may be recycle ratios that do indeed reduce COD removal efficiency. Bachmann et al. (1985) predicted that increased recycle rates at constant HRT (throughput) would lead to a decrease in COD removal efficiency. Further studies are required to determine the effect of recycle ratio on COD removal efficiency and to determine the optimal recycle ratio for treatment of ADF in ABR. It is evident however that the reduction of influent toxicity and substrate inhibition as pointed out by Barber and Stuckey (1999) makes it possible to achieve acceptable treatment efficiency at higher loading rates and does encourage two-phase digestion. Two-phase digestion (separation of acidogenesis and methanogenesis longitudinally through the reactor) may be considered an advantage or a disadvantage. Increased acid

concentrations may hamper methanogenesis, but increased acetic acid concentrations also provide an increased substrate concentration driving force, thereby increasing the substrate utilization rate.

Chapter 5

Summary of Results

A 1 % v/v ADF feed solution was successfully treated in ABR operated both with and without recycle at OLR varying between 4 and 11 g COD/$L_{reactor}$·d. The ABR operated without recycle achieved a minimum HRT of 27 h with an acceptable COD removal efficiency of 89 % at an OLR of 6.2 g COD/$L_{reactor}$·d, a SOLR of 0.30 g COD/g VSS·d and a U of 0.25 g COD_{rem}/g VSS·d. The ABR operated with a 6:1 recycle ratio achieved a minimum HRT of 17 h with an acceptable COD removal efficiency of 93 % at an OLR of 9.9 g COD/$L_{reactor}$·d, a SOLR of 0.35 g COD/g VSS·d and a U of 0.32 g COD_{rem}/g VSS·d. The SOLR were not found to vary significantly through most of the experimental period despite OLR increases due to biomass growth. It was also found that ABR treating ADF may be shut down for a period of months and then restarted with ease.

Although the pH in the ABR remained steady at 7.0 ± 0.2 the mere presence of VFA in a pH buffered solution were seen to inhibit methanogenesis. ABR compartmentalisation served to separate acidogenic and methanogenic activities longitudinally through the reactor, with the number of acidogenic bacteria highest at the inlet and dropping towards the outlet, allowing the reactor to behave as a naturally attenuated two-phase system without the associated control problems.

Recycle was found to reduce substrate toxicity effects through dilution and improved mixing through the ABR, thereby improving the U and allowing for greater throughput.

Biomass settling characteristics were found to remain constant throughout the experimental period with an average υ_{50} for the initial biomass of 49 ± 7 m/h and υ_{50} of 50 ± 5 m/h and, 47 ± 1 m/h for ABR with and without recycle respectively at the end of the experimental period. The volatile solids content of the granular biomass remained constant at 0.043 g VSS/mL throughout while the fraction of volatile to total solids remained constant at 0.74 g VSS/g TSS. Although the settling characteristics and content of the biomass remained constant, the granule size distribution did not.

As opposed to UASB treatment, where biomass losses have proven problematic, the ABR achieved SRT in excess of 250 d for the range of HRT studied and it was found that a method of biomass wastage would become necessary if a constant biomass

concentration within the ABR were desired. The net accumulated yield within the ABR was found to be of 0.007 g VSS/g COD_{rem} when the ABR was operated without recycle and of 0.016 g VSS/g COD_{rem} for the ABR operated with recycle. In this case the ABR operated without recycle maintained 50 % of the biomass yield whereas the ABR operated with recycle maintained 70 % of the biomass yield. Biomass losses were not consistent throughout the run period as the majority of losses occurred within short periods, or shock events. The increased mixing within the ABR operated with recycle is believed to have promoted detachment of gas bubbles from the anaerobic granules, thereby preventing accumulation of gases within the biomass bed and subsequently reducing the amount of shocks due to sudden release of biogases which would entrain losses of biomass.

The mixing study has shown that, hydrodynamically, ABR may be characterized as CSTR-in-series with low dead space and that the number of CSTRs could, for the purposes of modeling, correspond to the number of actual compartments.

The model studied by Xing et al. (1991) was found to yield first order reaction rate coefficients that were correlated with substrate concentration driving force. Xing et al. (1991) assumed that methanogenesis of acetic acid was the rate limiting step in anaerobic digestion and that the kinetic coefficients calculated thereby were therefore first order acetic acid reaction rate coefficients. Unfortunately, the assumption made by Xing et al. (1991), that COD measurements could be considered representative of the acetic acid concentration does not hold. Furthermore, since acetic acid is both created and consumed in anaerobic digestion and since high acetic acid concentration simultaneously inhibits and promotes methanogenesis, the assumption that the overall reaction rate is first order with either COD or acetic acid concentration does not hold. Since the coefficients calculated using the Xing et al. (1991) model can not account for this phenomenon no predictive correlation of k with HRT or OLR can be achieved. In the Xing et al. (1991) study, the relatively small COD concentration range and low VFA concentrations through the reactor would account for the relatively constant k values found therein. If the COD concentration differential had been greater, or the VFA concentrations higher, a variation in the k coefficients with OLR would have been

noticed and the use of an average k coefficient over a range of OLR would not have been appropriate.

U is independent of biomass concentration within the reactor or substrate concentration and is based upon the methanogenesis that occurs therein. It is thereby an appropriate indicator of the COD consumption rate within the ABR and is useful for comparing different treatment systems. U however, is still subject to variations due to extremes of substrate or VFA concentrations. A model based on U would not however be useful for predicting the COD out of the reactor or the intermediate COD concentrations since the outlet concentration is required in order to calculate the U. The effect of substrate-limited conditions in some reactor compartments as well as the conflict between the inhibitory effect of high VFA concentrations and an increase in the substrate concentration driving force, make it difficult to model ABR treatment of ADF at varying HRT and the Xing et al. (1991) CSTR-in-series model can not account for these phenomena.

The maximum attainable SOLR in ABR with acceptable COD removals may be limited by mass transfer rate considerations. An increase in the average diameter of the granular biomass may lead to a decrease in efficiency as mass transfer rate through the granule becomes limiting. Furthermore, mixing may not be adequate to replenish substrate supply near the granule. Overfull reactor compartments hinder fluidization and biomass wasting may improve ABR performance. A decrease in HRT may also reduce channelling and thereby improve fluidization of the bed and consequently the ABR may experience acceptable COD removals at shorter HRT.

Chapter 6

Conclusions

- A 1 % (v/v) ADF feed solution can be successfully treated at high rates in ABR operated both with and without recycle.
- Operation of an ABR treating a 1 % (v/v) ADF feed solution at a 6:1 recycle ratio allows for better COD treatment efficiency at shorter HRT and greater OLR than an ABR operated without recycle.
- A net positive biomass accumulation in ABR treating a 1 % (v/v) ADF feed solution was achieved without recycle at HRT between 39 h and 20 h and with recycle at HRT between 36 h and 14 h.
- ABR may be hydrodynamically characterized as CSTR-in-series with low dead space and the number of CSTRs could, for the purposes of modeling, correspond to the number of actual compartments.
- The CSTR-in-series model presented by Xing et al. (1991) does not hold for ABR treating a 1 % (v/v) ADF feed solution. The assumptions that COD measurements can be considered representative of the acetic acid concentration and that the overall reaction rate is first order with acetic acid concentration do not hold as acetic acid is both created and consumed in the ABR and since high acetic acid concentrations simultaneously inhibit and promote methanogenesis.

Chapter 7

Future Studies

- Develop a method to effectively maintain constant biomass concentrations within each compartment without disruption of the anaerobic environment within the ABR.
- ABR with high concentration of biomass in the first compartment and lower concentrations in the later compartments may prove ideal with the first compartment performing acidogenesis and the lower concentration of biomass providing polishing in the final compartments.
- Investigate methods of improving mixing within each compartment and to achieve even distribution of the influent feed across the width of the first compartment of the ABR.
- Compare the result achieved with the current ABR reactors to those achieved with ABR having narrower downflow sections and wider upflow sections.
- Investigate the effect of adding compartments.
- Investigate the effect of recycle ratio on COD removal efficiencies and determine the optimal recycle ratio for treatment of ADF in ABR.
- Determine whether reduced channelling or otherwise improved mixing would make it possible to achieve acceptable COD removal efficiencies of 1 % ADF feed at HRT less than 20 h without recycle and at HRT less than 14 h for ABR operated with a 1:6 recycle ratio.
- Investigate the variation of treatment efficiency with the size distribution of the biomass granules.
- Investigate modeling based on expanded beds in series.
- Investigate the treatment of dilute ADF wastewater at short HRT.

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Appendix A: Mixing Study Results

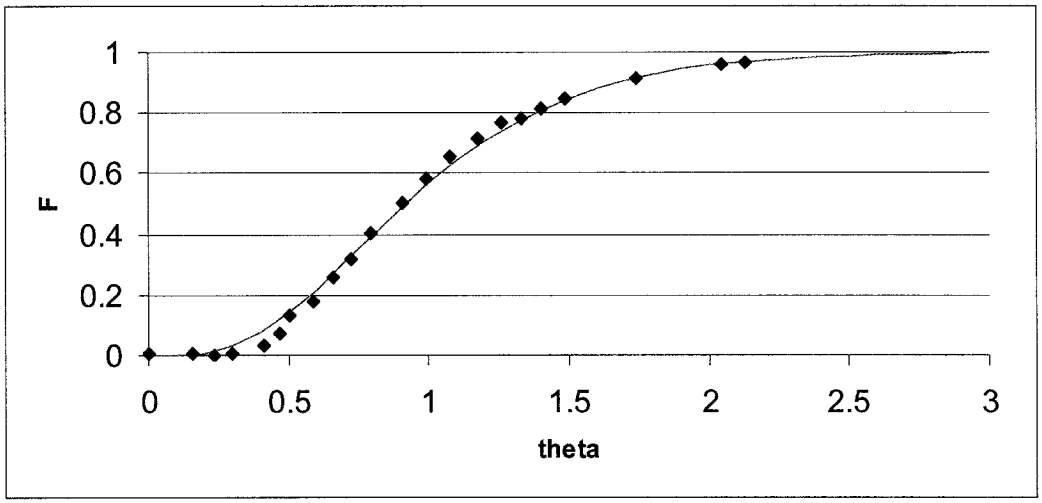

Figure A1: F curve for 6 h HRT with N = 4 model superimposed

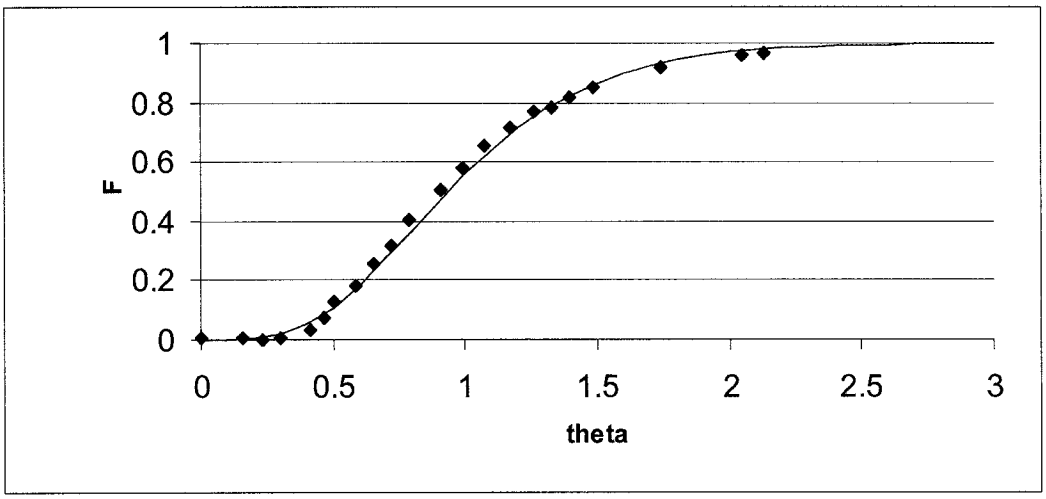

Figure A2: F curve for 6 h HRT with N = 5 model superimposed

Table A1: Comparison of model fits for 6 h HRT mixing test

F curve model	R^2
N = 4	0.93
N = 5	1.01

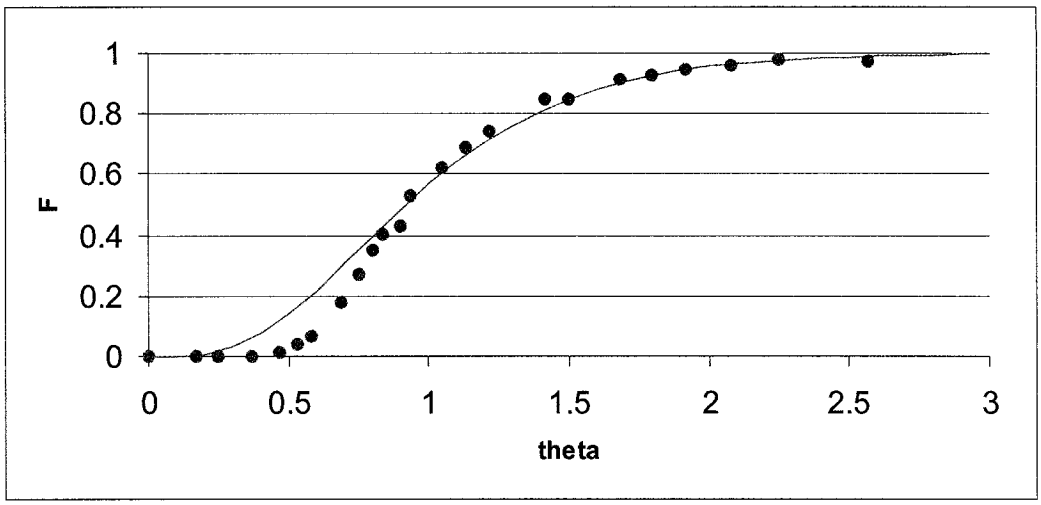

Figure A3: F curve for 1 h HRT with N = 4 model superimposed

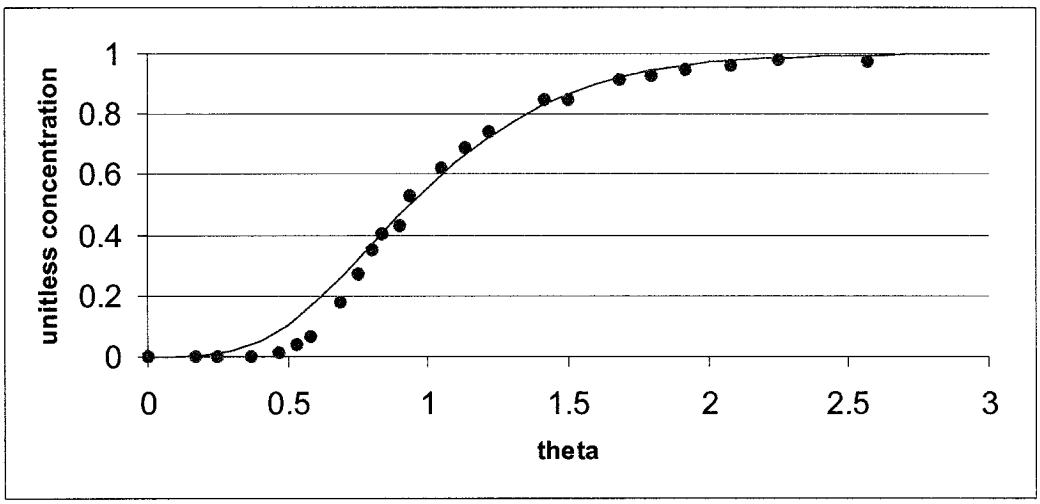

Figure A4: F curve for 1 h HRT with N = 5 model superimposed

Table A2: Comparison of model fits for 1 h HRT mixing test

F curve model	R^2
N = 4	0.85
N = 5	0.92

Note that a Residence Time Distribution (RTD) test is by its nature correlated, so that the correlation in the residual plots is not unexpected.

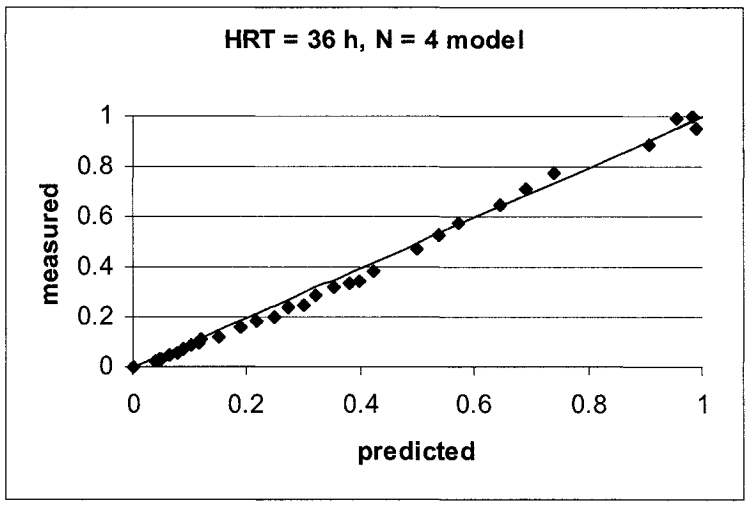

Figure A5: Residual plot for HRT of 36 h with N = 4 model

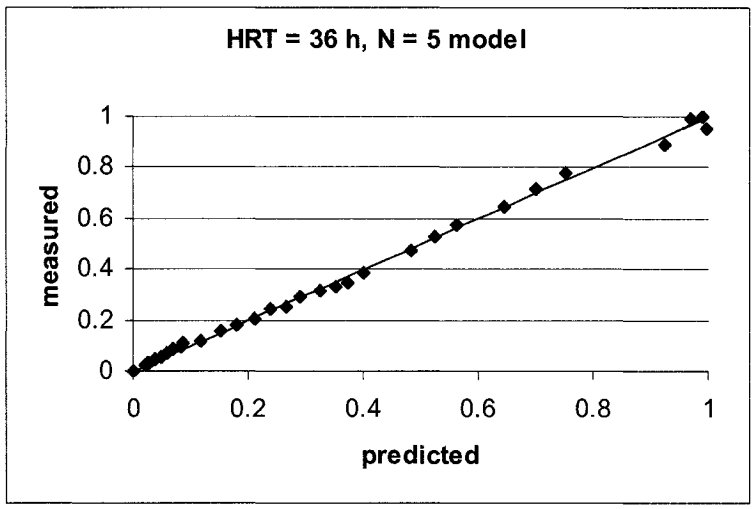

Figure A6: Residual plot for HRT of 36 h with N = 5 model

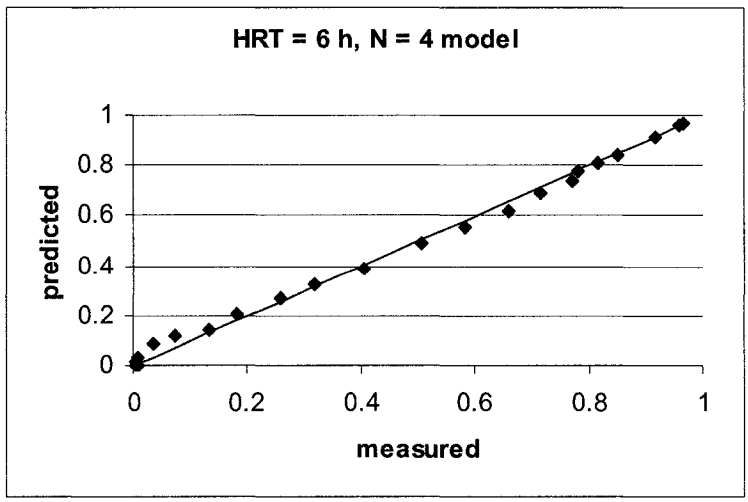

Figure A7: Residual plot for HRT of 6 h with N = 4 model

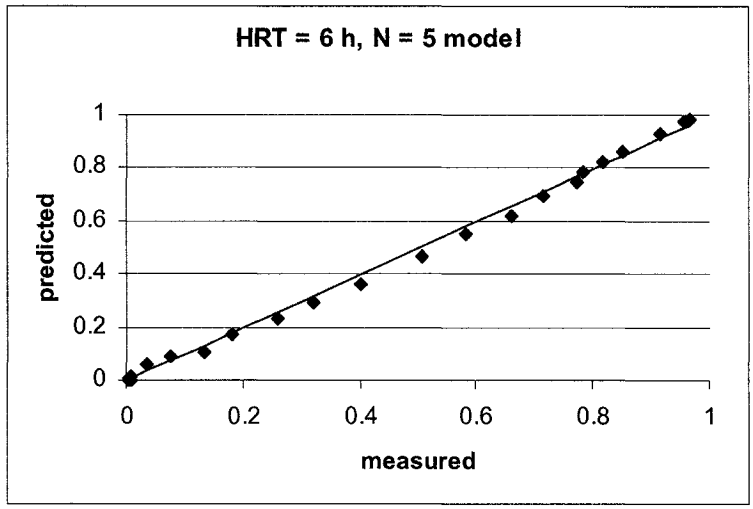

Figure A8: Residual plot for HRT of 6 h with N = 5 model

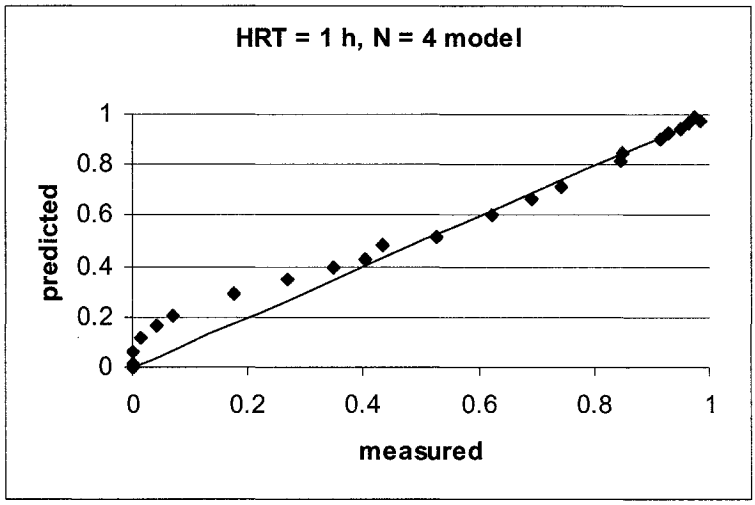

Figure A9: Residual plot for HRT of 1 h with N = 4 model

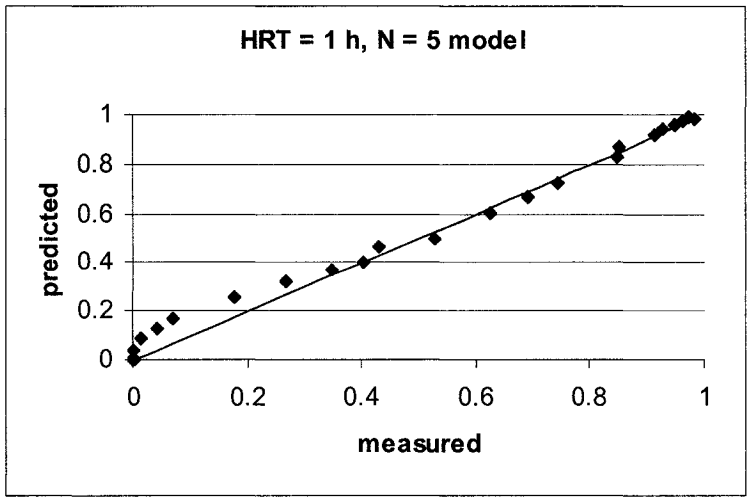

Figure A10: Residual plot for HRT of 1 h with N = 5 model

Appendix B: Statistics and Results

In order to determine 95 % confidence intervals (± 2 standard deviations) for the calculated results, each equation was linearized using Taylor Series expansion and then, knowing that

$$\mathrm{var}\left(\sum_{i=1}^{k} a_i y_i\right) = \sum_{i=1}^{k} a_i^{\,2}\,\mathrm{var}(y_i)$$

the variance, and thereby the standard deviation of the calculated results can be calculated from the variance of the individual measurements where the measurements are:

name	description	units
COD_{in}	COD into compartment	g COD
COD_{out}	COD out of compartment	g COD
G	biomass density	g/mL
HRT	hydraulic retention time	h
OLR	organic loading rate	g COD/L·d
R	recycle ratio	unitless
SOLR	specific organic loading rate	g COD/g VSS·d
U	specific substrate utilisation rate	g COD_{rem}/g VSS·d
V	volume of biomass	L
VSS	mass of biomass	g
V_{tot}	total volume	L
η	COD removal efficiency	%

Linearizations (where the numeral is the unit conversion factors):

$$VSS = G\,V(1000)$$

$$VSS \cong 1000\left[G_s V_s + (G - G_s)\frac{\partial GV}{\partial G}\bigg|_s + (V - V_s)\frac{\partial GV}{\partial V}\bigg|_s\right]$$

$VSS \cong 1000(G_s V_s + V_s G + G_s V)$, then since the variance of $G_s V_s = 0$

$\mathrm{var}(VSS) = (1000V_s)^2\,\mathrm{var}\,G + (1000G_s)^2\,\mathrm{var}\,V$ and $G_s = 0.043\,g/mL$ and $\mathrm{var}(G) = 1.3\times10^{-5}$

Similarly:

$$\eta = \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100\%$$

$$\eta \cong \left[\left(COD_{in} - COD_{in_S}\right) \frac{\partial\left(\frac{COD_{in} - COD_{out}}{COD_{in}}\right)}{\partial COD_{in}} + \left(COD_{out} - COD_{out_S}\right) \frac{\partial\left(\frac{COD_{in} - COD_{out}}{COD_{in}}\right)}{\partial COD_{out}} + \left(\frac{COD_{in} - COD_{out}}{COD_{in}}\right)\Bigg|_S \right]$$

$$\operatorname{var}\eta \cong \left(\frac{COD_{out}}{COD_{in}^{\,2}}\right)\Bigg|_S^2 \operatorname{var} COD_{in} + \left(\frac{-1}{COD_{in}}\right)\Bigg|_S^2 \operatorname{var} COD_{out}$$

and,

$$OLR = \frac{6 \times 10^{-3}}{HRT} COD_{in}$$

$$\operatorname{var} OLR \cong \left(\frac{6 \times 10^{-3}}{HRT}\right)^2 \operatorname{var} COD_{in} .$$

For the biomass specific results, the variances can be found from:

$$SOLR = \left(\frac{0.0462}{HRT}\right)\left(\frac{COD_{in}}{VSS}\right)$$

$$SOLR \cong \left(\frac{0.0462}{HRT}\right)\left[\frac{1}{VSS_s} COD_{in} + \left(\frac{-COD_{in}}{VSS^2}\right)\Bigg|_s VSS\right]$$

$$\operatorname{var} SOLR \cong \left(\frac{0.0462}{HRT \cdot VSS_s}\right)^2 \operatorname{var} COD_{in} + \left[\left(\frac{-COD_{in}}{VSS^2}\right)\Bigg|_s \cdot \frac{0.0462}{HRT}\right]^2 \operatorname{var} VSS$$

and,

$$U = \frac{0.0462}{HRT}\left(\frac{COD_{in} - COD_{out}}{VSS}\right)(1 + R)$$

$$\operatorname{var} U \cong \left(\frac{0.0462 \cdot (1+R)}{HRT \cdot VSS}\right)\Bigg|_s^2 \operatorname{var} COD_{in} + \left(\frac{-0.0462 \cdot (1+R)}{HRT \cdot VSS}\right)\Bigg|_s^2 \operatorname{var} COD_{out}$$

$$+ \left(\frac{0.0462}{HRT} \cdot \frac{-COD_{in} + COD_{out}}{VSS^2} \cdot (1+R)\right)\Bigg|_s^2 \operatorname{var} VSS$$

And finally, for the total biomass volume,

$$V_{tot} = V_1 + V_2 + V_3 + V_4$$

$$\text{var}\, V_{tot} \cong \text{var}\, V_1 + \text{var}\, V_2 + \text{var}\, V_3 + \text{var}\, V_4 .$$

Results, where the value ± 2 standard deviations is the 95 % confidence interval:

Table B1: COD measurements in ABR without recycle

HRT	36 h		24 h		20 h	
COD (mg/L)	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	2054	417	5480	646	6549	781
compartment 2	210	26	3655	480	5979	809
compartment 3	113	11	1716	229	4568	770
compartment 4	93	4	749	109	3541	731
feed	7000	417	7000	410	6988	772

Table B2: Calculated COD removal efficiency for ABR without recycle

HRT	36 h		24 h		20 h	
COD removal (%)	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	71	0.06	22	0.10	6	0.15
compartment 2	90	0.02	33	0.12	9	0.16
compartment 3	46	0.08	53	0.09	24	0.17
compartment 4	18	0.09	56	0.09	22	0.21
total	99	0.00	89	0.02	49	0.12

Table B3: VSS measurements in ABR without recycle

HRT	36 h		24 h		20 h	
VSS (g)	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	166	18	197	27	187	25
compartment 2	171	23	175	24	197	28
compartment 3	187	31	195	28	202	30
compartment 4	156	27	179	27	170	25
total	679	97	746	104	756	104

Table B4: Calculated OLR for ABR without recycle

HRT	36 h		24 h		20 h	
OLR (g/L.d)	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	17.23	0.0064	24.89	0.0091	33.54	0.0232
compartment 2	5.06	0.0064	19.49	0.0143	31.43	0.0234
compartment 3	0.52	0.0004	13.00	0.0107	28.70	0.0243
compartment 4	0.28	0.0002	6.10	0.0051	21.93	0.0231
total	4.31	0.0256	6.22	0.0365	8.39	0.0927

Table B5: Calculated SOLR for ABR without recycle

HRT	36 h		24 h		20 h	
SOLR (g/g.d)	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	0.8006	0.0162	0.9743	0.0141	1.3803	0.0238
compartment 2	0.2277	0.0049	0.8581	0.0152	1.2305	0.0213
compartment 3	0.0213	0.0003	0.5125	0.0086	1.0920	0.0191
compartment 4	0.0138	0.0002	0.2627	0.0041	0.9953	0.0181
total	0.1954	0.0430	0.2570	0.0577	0.3417	0.0880

Table B6: Calculated U for ABR without recycle

HRT	36 h		24 h		20 h	
U (g/grem.d)	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	0.5657	0.0131	0.2115	0.0089	0.0867	0.0179
compartment 2	0.2045	0.0047	0.2857	0.0112	0.1071	0.0169
compartment 3	0.0098	0.0002	0.2719	0.0068	0.2577	0.0162
compartment 4	0.0025	0.0001	0.1481	0.0033	0.2238	0.0175
total	0.1928	0.0425	0.2295	0.0524	0.1686	0.0748

Table B7: COD measurements in ABR with recycle

HRT	36 h		24 h		20 h		17 h		14 h	
COD (mg/L)	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	568	19	952	71	737	247	1196	264	2804	264
compartment 2	298	8	467	118	688	95	851	271	2688	199
compartment 3	164	6	213	12	402	99	573	294	2408	179
compartment 4	139	19	110	6	329	97	508	331	2255	234
feed	6200	19	7000	48	7000	133	7000	227	6296	295
COD into comp 1	948	17	1375	48	1540	133	1373	288	2516	295

Table B8: Calculated COD removal efficiency for ABR with recycle

HRT	36 h		24 h		20 h		17 h		14 h	
COD removal (%)	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	40	0.02	31	0.06	52	0.17	13	0.27	4	0.11
compartment 2	48	0.02	51	0.13	7	0.34	29	0.28	4	0.11
compartment 3	45	0.03	54	0.12	41	0.17	33	0.41	10	0.09
compartment 4	15	0.12	48	0.04	18	0.31	11	0.74	6	0.12
total	98	0.00	98	0.00	95	0.01	93	0.05	64	0.04

Table B9: VSS measurements in ABR with recycle

HRT	36 h		24 h		20 h		17 h		14 h	
VSS (g)	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	163	25	188	25	232	55	234	25	269	36
compartment 2	163	27	168	27	228	35	286	38	262	36
compartment 3	161	27	170	29	174	27	233	35	254	39
compartment 4	152	25	153	25	169	33	192	30	197	29
total	639	103	679	104	802	128	945	126	983	140

Table B10: Calculated OLR for ABR with recycle

HRT	36 h		24 h		20 h		17 h		14 h	
OLR (g/L.d)	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	2.53	0.0003	5.50	0.0012	7.39	0.0040	7.76	0.0102	19.16	0.0088
compartment 2	1.52	0.0003	3.81	0.0018	3.54	0.0074	6.75	0.0093	19.23	0.0113
compartment 3	0.80	0.0001	1.87	0.0030	3.30	0.0028	4.81	0.0096	18.43	0.0085
compartment 4	0.44	0.0001	0.85	0.0003	1.93	0.0030	3.23	0.0104	16.51	0.0077
total	4.13	0.0013	7.00	0.0048	8.40	0.0159	9.88	0.0321	10.79	0.0505

Table B11: Calculated SOLR for ABR with recycle

HRT	36 h		24 h		20 h		17 h		14 h	
SOLR (g/g.d)	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	0.1190	0.0015	0.2249	0.0033	0.2456	0.0057	0.2552	0.0070	0.5477	0.0084
compartment 2	0.0716	0.0008	0.1749	0.0022	0.1197	0.0035	0.1816	0.0041	0.5644	0.0087
compartment 3	0.0380	0.0004	0.0848	0.0017	0.1461	0.0022	0.1589	0.0041	0.5587	0.0073
compartment 4	0.0222	0.0003	0.0427	0.0005	0.0883	0.0020	0.1299	0.0052	0.6456	0.0087
total	0.1991	0.0364	0.3176	0.0614	0.3227	0.0705	0.3221	0.0725	0.3383	0.0720

Table B12: Calculated U for ABR with recycle

HRT	36 h		24 h		20 h		17 h		14 h	
U (g/grem.d)	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev	value	2 std dev
compartment 1	0.3572	0.0047	0.5194	0.0115	0.9598	0.0334	0.2473	0.0553	0.0000	0.0390
compartment 2	0.2554	0.0032	0.6682	0.0151	0.0607	0.0246	0.3927	0.0350	0.1750	0.0392
compartment 3	0.1280	0.0016	0.3465	0.0114	0.4544	0.0161	0.3899	0.0404	0.4362	0.0298
compartment 4	0.0250	0.0014	0.1551	0.0022	0.1210	0.0157	0.1106	0.0553	0.3077	0.0428
total	0.1946	0.0355	0.3126	0.0604	0.3075	0.0674	0.2987	0.0703	0.2171	0.0508

Appendix C: Acetoclastic Activity Tests

Acetoclastic activity tests were performed on biomass samples taken from each lower port in each reactor after the first steady state condition, then twice more, once at the midpoint of the testing period and once again at the end of the testing period. The acetoclastic activity test were not found to be representative of specific substrate utilization rate.

Table C1: Acetoclastic activity after 39 h HRT ABR without recycle

Dec. 6, 2001 ABR without recycle				
acetoclastic activity				
g AC/g VSS/d				
sample	a	b	average	+ or -
A3	0.21			
A7	0.15			
A11	0.08			
A15	0.02			

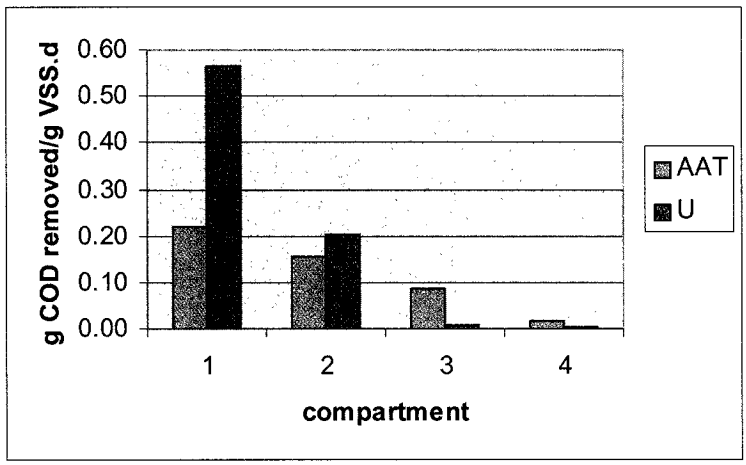

Figure C1: Comparison on acetoclastic activity and U after 39 h HRT ABR without recycle

Table C2: Acetoclastic activity after 27 h HRT ABR without recycle

Apr. 12, 2002 ABR without recycle				
acetoclastic activity				
g AC/g VSS/d				
sample	a	b	average	+ or -
A3		0.04	0.04	
A7	0.18	0.16	0.17	0.01
A11	0.06	0.13	0.10	0.03
A15	0.05	0.05	0.05	0.00

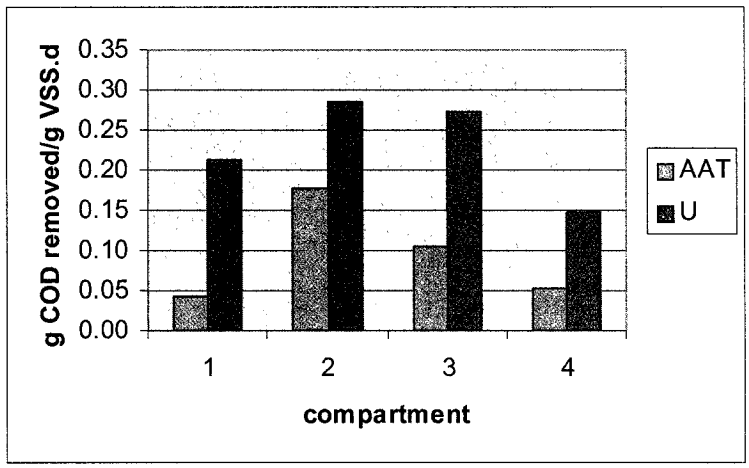

Figure C2: Comparison on acetoclastic activity and U after 27 h HRT ABR without recycle

Table C3: Acetoclastic activity after 20 h HRT ABR without recycle

May 22, 2002 ABR without recycle				
acetoclastic activity				
g AC/g VSS/d				
sample	a	b	average	+ or -
A3	0.18	0.02	0.18	
A7	0.16	0.09	0.12	0.04
A11	0.27	0.19	0.23	0.04
A15	0.21	0.20	0.20	0.00

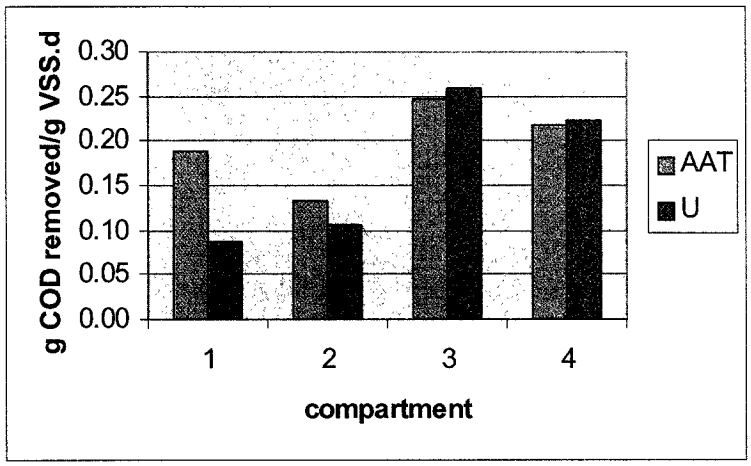

Figure C3: Comparison on acetoclastic activity and U after 20 h HRT ABR without recycle

Table C4: Acetoclastic activity after 24 h HRT ABR with recycle

Dec. 1, 2001 ABR with recycle				
acetoclastic activity				
g AC/g VSS/d				
sample	a	b	average	+ or -
B3	0.13		0.13	
B7	0.30	0.29	0.29	0.01
B11	0.30	0.28	0.29	0.01
B15	0.17	0.19	0.18	0.01

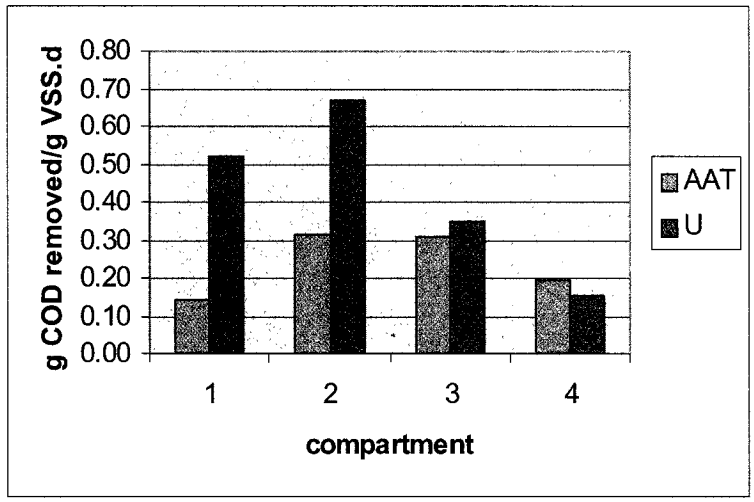

Figure C4: Comparison on acetoclastic activity and U after 24 h HRT ABR with recycle

Table C5: Acetoclastic activity after 20 h HRT ABR with recycle

Apr. 12, 2002 ABR with recycle				
acetoclastic activity				
g AC/g VSS/d				
sample	a	b	average	+ or -
B3	0.13		0.13	
B4	0.11		0.11	
B7	0.12	0.16	0.14	0.02
B11	0.13	0.16	0.15	0.02
B15	0.07	0.06	0.07	0.00

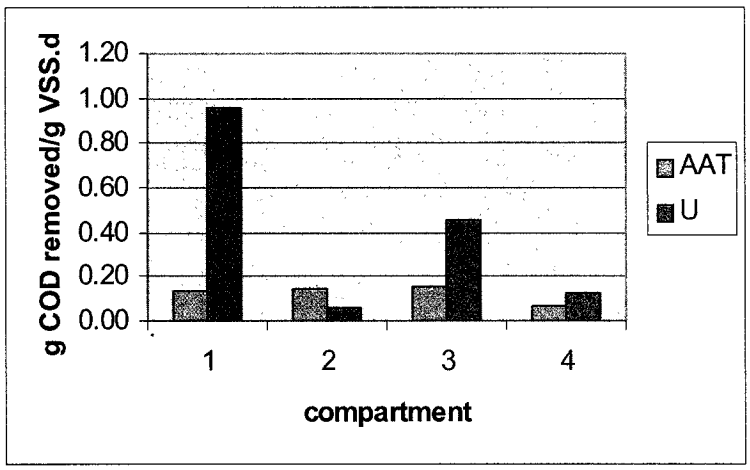

Figure C5: Comparison on acetoclastic activity and U after 20 h HRT ABR with recycle

Table C6: Acetoclastic activity after 14 h HRT ABR with recycle

May 22, 2002 ABR with recycle				
acetoclastic activity				
g AC/g VSS/d				
sample	a	b	average	+ or -
B3	0.13	0.14	0.14	0.01
B4	0.15		0.15	
B7	0.21	0.21	0.21	0.00
B8	0.21		0.21	
B11	0.28	0.26	0.27	0.01
B12	0.24		0.24	0.00
B15	0.17	0.20	0.19	0.01

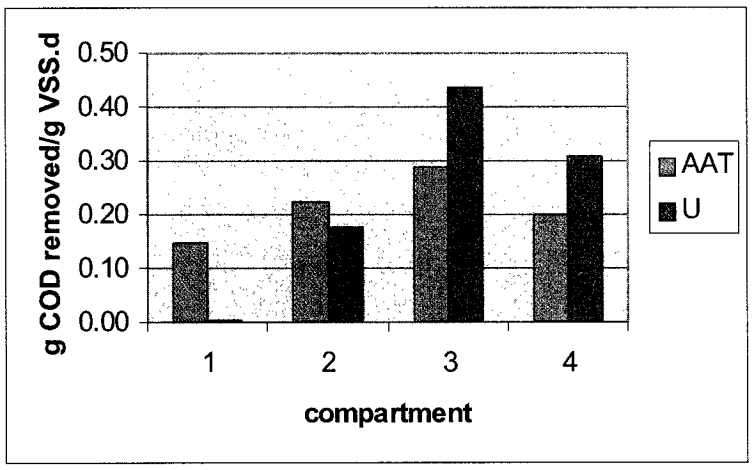

Figure C6: Comparison on acetoclastic activity and U after 14 h HRT ABR with recycle