Advanced Chemical Separation Using Foam Fractionation

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Abstract

Foam fractionation is a separation process by which enriched solutions of surface active molecules can be obtained from solution. Reflux is the process of partially returning the product to enhance enrichment. The use of controlled reflux has not been investigated in depth. The primary aim of this project was to achieve and investigate the use of controlled reflux on foam fractionation.

A foam fractionation column was designed, constructed and commissioned to overcome previous problems with achieving reflux. The column was operated with a surfactant called cetylpyridinium chloride (CPC) under a variety of continuous conditions. Measurements of concentration and liquid hold up were obtained under steady state conditions with and without reflux. Reflux is shown to significantly enhance the enrichment of the product. Dispersion of a salt tracer was also measured using conductivity probes to gain insight into the separation process.

Contents

1 Introduction

The property of surface active molecules (surfactants) to stabilise foams can be used in a separation process called foam fractionation. Foams are made up of a two-phase system comprising gas cells surrounded by liquid. Foam fractionation has the potential to cut the cost of producing biosurfactants by an order of magnitude.

The liquid content of foams depends on the conditions that created them. If a foam is too wet it can lose its rigidity and be replaced by a bubbly liquid. Drier foams have liquid films between the gas bubbles, and tend to be polyhedral in shape. The channels formed by the intersection of these films form a network through the foam and are called Plateau borders. This applies to the foam used in this project. Figure 1.1 shows an example of a Plateau border network. (Weaire *et al* 1999)

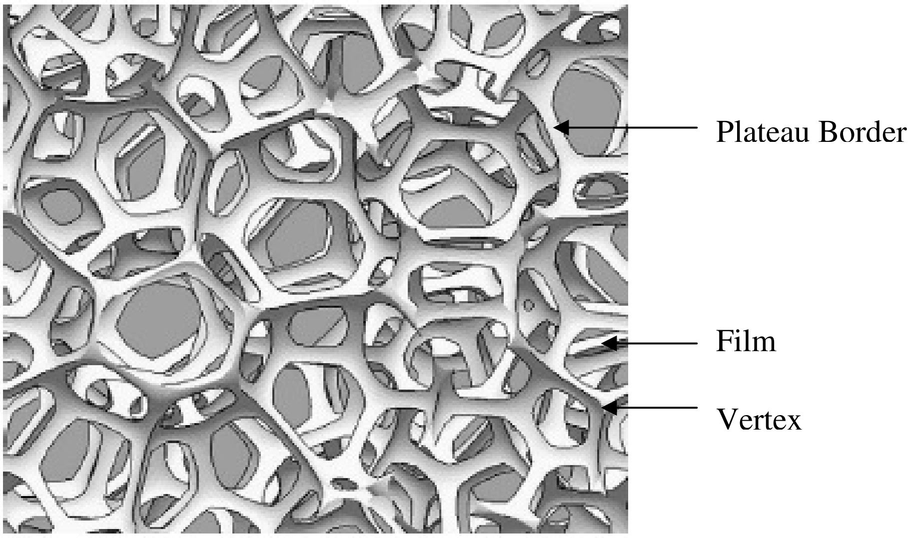

Figure 1.1 Simulation of Plateau borders in a foam (Brakke (1992) in Lee *et al* 2005)

Surfactant molecules have a hydrophilic end and a hydrophobic end; one end likes to be within liquid while the other prefers to be in a gas. By sparging air through a solution containing surfactant the surfactant molecules adsorb to the surface of the air bubbles. When the bubbles reach the surface of the liquid the foam is formed. The surfactants sit on the gas liquid interface of the bubbles, and tend to stabilise the foam.

Foam fractionation works because of the surfactants adsorbing onto the bubble surface. Liquid from the feed is entrained within the foam network (interstitial liquid). Interstitial liquid drains through the Plateau borders due to gravity; within a column of foam this leads to the foam becoming drier as the column is ascended. The foam is broken at the top of the column releasing the gas and yielding the foamate. The entrained liquid and surfactant that was on the surface of the gas bubbles forms the top product. Since this is composed of both interstitial liquid at the feed concentration plus adsorbed surfactant, the foamate is enriched in surfactant.

1.1 Foam Fractionation History in Oxford

A large volume of work has been carried out on foam fractionation by previous fourth year project students. Recent work has included the investigation of multi-stage design (Pearson 2004) and the effect of riser geometry on column performance (Swain 2005, Oyinloye 2006).

The projects in previous years have successfully run batch and continuous columns and measured conditions in the columns. They have not managed to successfully introduce controlled reflux to a foam fractionation column or measure the rate of foamate produced during continuous operation. Limitations due to the column design (outlined in Section 3.1) meant that it was not possible to control reflux and a new design and column was therefore needed.

1.2 Project Aims

The aims of the project were to

- Design new equipment (carried out as part of a separate studentship)
- Set up and establish consistent measurements and test procedure for the new equipment
- Successfully introduce a controlled amount of reflux into the column

- Investigate the effects of reflux on the enrichment of surfactant for continuous and stable operation.
- Obtain a set of experimental results for the column's concentration profile and liquid hold up.
- Measure dispersion of liquid in the column
- Use the experimental behaviour to analyse the column's performance.

1.3 Report

This report will introduce the theory involved in foam fractionation. It will then cover the design and the development of the apparatus used. The methods and results obtained for the experiments will be reported and it will be shown that reflux enhances enrichment, with the extent of enrichment depending upon the reflux ratio.

2 Theory and Literature Review

2.1 Foam fractionation Theory

As described in Section 1 foam fractionation consists of a bulk solution below a riser. This section explains the fundamental processes behind its operation and modelling approaches.

2.1.1 Surface Excess - Γ

Surface excess is the surface concentration of the adsorbed surfactant. The value of the surface excess can be calculated from the Gibbs Absorbtion equation (Gibbs 1928 discussed in Lemlich 1972).

$$d\gamma_i = -RT\sum \Gamma_i d\, ln\, a_i \qquad [2.1]$$

Where γ is surface tension, R is the gas constant, T is absolute temperature and a is the activity of the ith component. Surface excess has units of moles/area^2.

Equation 2.1 is difficult to apply in practice as the surface tension needs to be measured very accurately and the value of the activity is often unknown. For low concentrations of surfactant the activity coefficient can be taken to be constant and equal to the concentration of the bulk solution. The equation can be simplified to

$$\Gamma = \frac{-1}{nRT}\frac{d\gamma}{d\ln C} \qquad [2.2]$$

Where n is the ionic charge of the surfactant (2 for CPC) and C is the concentration of the bulk solution.

The critical micelle concentration (CMC) is the concentration above which a surfactant no longer lowers surface tension and the addition of additional surfactant goes towards the formation of micelles; aggregates of surfactant molecules. A low concentration of surfactant would be considered to be below the CMC. The bulk solution in this project will be slightly above the CMC and the equation should not hold. However, Lemlich (1968) states that the value for surface excess essentially applies above the CMC as the bulk is saturated with a monolayer of surfactant molecules above the CMC and the creation of micelles does not affect this.

Equation 2.2 indicates that the surface excess can be calculated by considering a plot of surface tension against concentration. The calculation of surface excess is shown in Section 5.2.

2.1.2 Liquid Hold Up - ε

Liquid hold up is the fraction of liquid volume in the foam when compared to the total foam volume. As the foam rises up the column liquid drains through the foam network, leading to a decrease in liquid hold up. The liquid hold up tends to be fairly constant higher up a column than compared to near the base.

2.1.3 Reflux ratio - R

The reflux ratio is the ratio of the return flow rate of top product to the flow of top product out. A reflux ratio of zero means there is no reflux and a reflux ratio of infinity means that all the top product is being returned to the column.

Reflux is useful because it can be used to obtain higher enrichment of top product. Yamagiwa *et al* (2001) has also shown that reflux can be used to increase the concentration of top product when the feed concentration is so high that without reflux the top product has the same concentration as the feed. Reflux enriches the top product because there is mass transfer between the reflux and the rising liquid, leading to an enhanced concentration gradient in the column; this is analogous to reflux in distillation.

2.1.4 Column Operation

Analysis of a foam fractionation column is similar to that of a distillation column. Using an analogy of distillation with entrainment a material balance can be carried out over the column and an operating line established (Lemlich 1972). The analogy is that the rising bubble surfaces correspond to vapour and the upward flow of interstitial liquid is the entrained liquid. Interstitial liquid draining through the foam corresponds to the downflow within a distillation column.

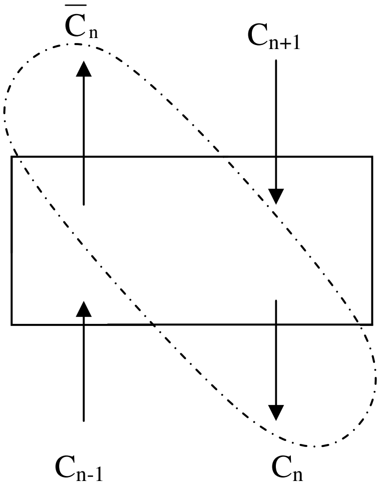

Figure 2.1 An equilibrium stage

Figure 2.1 shows an equilibrium stage. An equilibrium or theoretical stage is where the two leaving streams are in equilibrium with each other (Darton 2006). The streams in equilibrium are circled on Figure 2.1. The effective concentration of solute within the rising stream of the column can be defined by the equilibrium relationship (Lemlich 1968).

$$\overline{C}_n = C_n + \frac{GS\Gamma}{U} \qquad [2.3]$$

Where *C* is the concentration of the interstitial liquid in the rising stream, *G* is the gas flow rate, *S* is the ratio of bubble surface to bubble volume. *U* is the rate of interstitial liquid upflow and Γ is the surface excess, which is assumed to be in equilibrium with *C*. Identifying the value of *U* is difficult because there is not a direct way to measure its value. Some approaches for calculating it are discussed in Section 2.3

Figure 2.2 shows a mass balance over the whole column and over the top section of the column. The flow into the column has a flowrate *f* and concentration C_f. The flow out the bottom is *w,* with concentration C_w. *R* is the reflux ratio, *d* the flowrate of top product and C_d the top product concentration.

For the balance over the top of the column $\overline{C_n}$ is the concentration in the rising stream, *u* is the flow of entrained liquid upwards and *L* is the flow of liquid draining downwards.

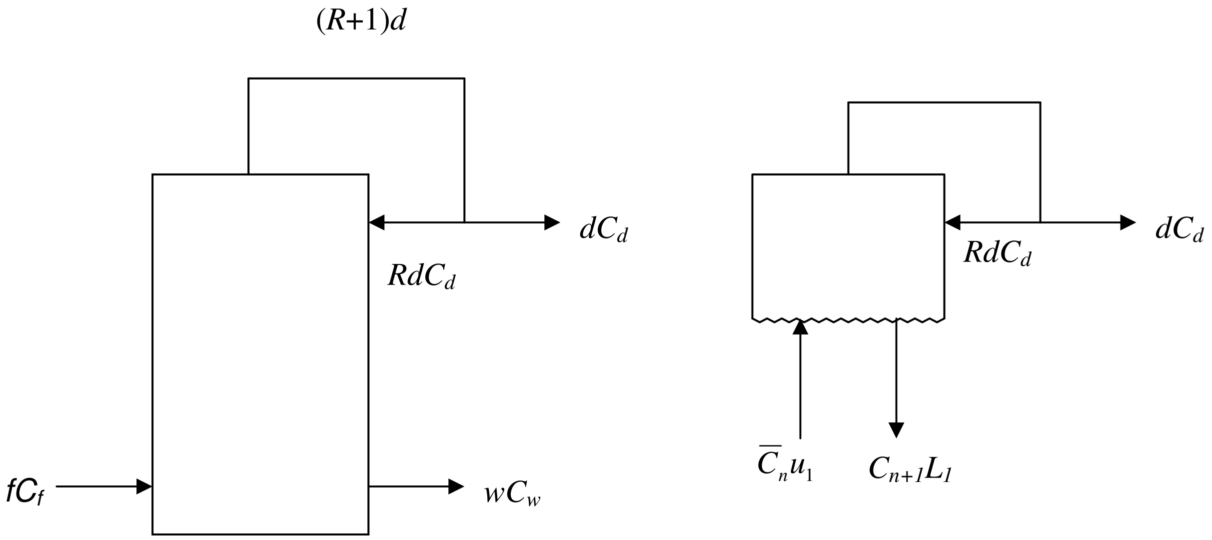

Figure 2.2 Material balance over column and top section of column (based on Swain 2005)

From a mass balance the operating line is

$$\overline{C}_n = \frac{R}{R+1} C_{n+1} + \frac{1}{R+1} C_D \qquad [2.4]$$

The assumptions for this analysis are that the column is operating under continuous steady state conditions, that the flow of liquid up and down the column is constant and that there is no internal reflux in the column. The second two assumptions are the least accurate, drainage due to gravity will mean the flow up and down the column of liquid is not constant and coalescence will lead to internal reflux. Coalescence is when the film on a foam bubble thins. This leads to two bubbles merging into a larger bubble. The rupture of the films will lead to absorbed surfactant being released, causing enrichment. However severe coalescence leads to collapse of the foam which would prevent the foam reaching the end of the column. The more stable the foam within the column the less coalescence will occur.

From the equilibrium line and operating line a graphical calculation of the number of theoretical stages can be carried out. The liquid pool at the bottom of the column is generally considered to be one theoretical stage (Lemlich 1972).

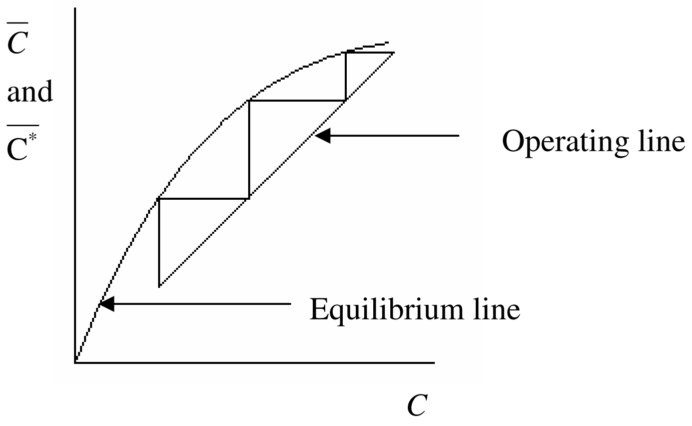

Figure 2.3 Example of a graphical stagewise calculation (based on Lemlich 1972)

2.1.4.1 Number of Theoretical Transfer Units (NTU)

Lemlich (1972) gives an analytical method for analysing the number of theoretical stages in the column based upon the rising stream.

$$NTU = \int_{C_w^*}^{C_q} \frac{d\overline{C}}{\overline{C}^* - \overline{C}} \qquad [2.5]$$

Where $\overline{C}^*$ is the effective concentration $\overline{C}$ in equilibrium with C_w and C_q is the concentration of the top product. This equation can be integrated to give

$$NTU = R\ln\left[\frac{RGS\Gamma(f-d)}{(R+1)GS\Gamma(f-d)-(R+1)fd(C_d-C_f)}\right] \qquad [2.6]$$

Where f is the volumetric flow rate of feed and d is the volumetric flow rate of top product.

2.2 Dispersion

Dispersion is a form of mass transfer where mass spreads out from an area of high concentration to low concentration. Lee *et al* (2005) outline two mechanisms for dispersion in foams, Plateau border dispersion and geometric dispersion. Geometric dispersion is due to the random movement of molecules through the drainage channels. Plateau border dispersion occurs because of velocity profiles in the Plateau borders. The velocity profiles occur because the liquid gas interfaces which form the walls of the Plateau borders cause a degree of shear. The velocity at these walls can therefore be quite different to that towards the centre of a Plateau border. Plateau border dispersion is similar to that seen in packed beds with back mixing. The back mixing here is the liquid reflux flowing down the riser.

Levenspiel (1999) describes dispersion through an ideal pulse of tracer entering a fluid in a vessel. The pulse of tracer then spreads out as it passes through the vessel and can be characterised as a diffusion like process superimposed on plug flow.

Stevenson *et al* (2003) state that tracer dispersion is due to two mechanisms, foam drainage and liquid elements taking a random path through the network of Plateau borders (geometric dispersion). When the tracer is injected into the foam the liquid hold up is greatly increased and the local value of liquid hold up now consists of the value of the excess hold up and the original liquid hold up. Foam drainage dispersion then occurs to remove the excess liquid hold up and return the value of liquid hold up to the original value. This is a relatively short process; once it has completed dispersion continues through Plateau border dispersion.

2.2.1 Dispersion Coefficient - D

The dispersion coefficient, D is a method of characterising the degree of backmixing in flow. As the dispersion coefficient tends to zero the flow becomes plug flow. As it tends to infinity the flow becomes fully mixed. Lemlich (1972) states that deviations from plug flow reduce the efficiency of the column because it destroys the countercurrent flow in the column. This reduction in efficiency will be seen as a reduction in the number of theoretical stages. Levenspiel (1999) suggests a method for calculating the dispersion coefficient based on a model for a packed bed with back mixing. The governing differential equation is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad [2.7]$$

Where D is the axial dispersion coefficient and C is concentration. This can be expressed in a dimensionless form using the substitutions

$$z = \frac{(ut + x)}{L} \text{and} \theta = \frac{tu}{L} \qquad [2.8]$$

Equation 2.7 then becomes

$$\frac{\partial C}{\partial \theta} = \left(\frac{D}{uL}\right)\frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \qquad [2.9]$$

$\frac{D}{uL}$ is the vessel dispersion number and is a dimensionless group that expresses the degree of axial dispersion. The greater the dispersion number the greater the dispersion. The equation can be solved for large deviation from plug flow $\left(\frac{D}{uL} > 0.01\right)$ and for smaller amounts of dispersion. The dispersion experiments in Section 5.5 have large amounts of dispersion. As there is undisturbed flow at the sampled points the boundary conditions are open vessel. Levenspiel (1999) outlines the solution to the governing differential equation for open vessel boundary conditions, which were first derived by Levenspiel and Smith (1957):

$$C_\theta = \frac{1}{\sqrt{4\pi\left(\frac{D}{uL}\right)}}\exp\left[\frac{-(1-\theta)^2}{4\theta\left(\frac{D}{uL}\right)}\right] \qquad [2.10]$$

The mean and variance are given by

$$\theta_C = 1 + 2\left(\frac{D}{uL}\right) \qquad [2.11]$$

$$\sigma^2 = 2\frac{D}{uL} + 8\left(\frac{D}{ul}\right)^2 \qquad [2.12]$$

By measuring the concentration of a tracer injected into the riser (test procedure outlined in Section 4.6.4) a plot of C against t can be plotted and the mean and variance calculated. From this the dispersion coefficient can then be found.

2.3 Other Analysis

There have been empirical approaches to modelling the number of stages within a foam fractionation column. One recent approach was by Stevenson *et al* (2006) and uses an equilibrium stage approach to model the performance of continuous foam fractionation with reflux. The analysis relies on the knowledge of constants that are particular to a surfactant system. Forced drainage experiments can be used to calculate these (Stevenson 2006). The forced drainage experiments were not successfully carried out in this project so the theory will not be set out.

3 Apparatus Design, Construction and Commissioning

Previous work on foam fractionation within the Department of Engineering Science at the University of Oxford has had difficulties in achieving controlled reflux to the column and in obtaining a top product, which could be measured. The primary aim of the design of new equipment was to eliminate these problems.

The initial design work was done during the summer vacation, whilst employed on a studentship. The foam columns were then commissioned before the beginning of Michaelmas 2006 and arrived at the end of October.

3.1 Foam Fractionation Column Design

The primary criteria for the column design were:

1. Reflux should be controllable
2. Samples should be able to be taken from inside the column
3. It should be possible to have a multi-stage process

The reason that controllable reflux has not been achievable for the previous projects has been to capillary suction. Capillary suction is when a foam comes into contact with a pool of liquid. Liquid from the pool is pulled into the foam channels and the height of the liquid pool decreases. This is shown in Figure 3.1. Previous designs (Swain 2005, Pearson 2004) have used vertical columns, with the top product going into a pool surrounding the top of the riser. As complete foam breakage has always proved difficult to achieve this has led to the foam coming out of the riser and covering the pool containing the top product. Capillary suction has then removed some of the top product, which then drains back down the column. This means that some reflux is occurring, but the amount cannot be controlled or measured.

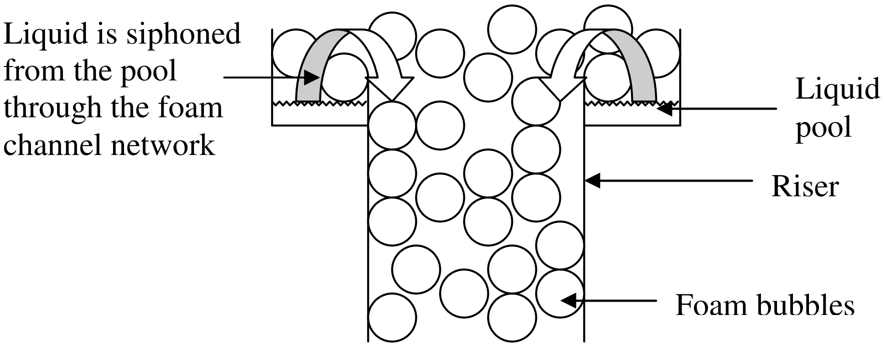

Figure 3.1 Capillary suction in the previous column

To prevent this it was decided to try a curved column. The concept was that the capillary suction would not lead to liquid being drained from the top product back down the column. Instead although there would still be capillary suction taking place the liquid would drain back into the top product container. The disadvantage of this approach is that the geometry makes the column more difficult to model. The initial design was produced using the Engineering department's rapid prototyping machine and is shown in Figure 3.2.

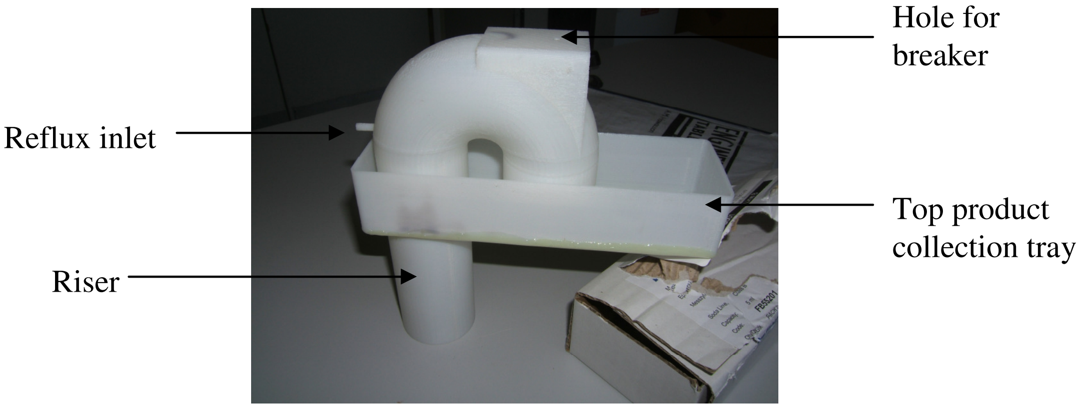

Figure 3.2 Prototype of foam fractionation column

It was designed with the top product tray being part of the column. A shaft with a mechanical foam breaker was fitted through the smaller vertical section and attached to a small electric motor. Tests with the prototype indicated that the design removed the problem with capillary suction.

The use of a tray that was significantly longer than the column diameter for collecting the top product was so that a second column could be placed over the clear side of the tray, allowing for a second stage of foam to be produced from the top product and therefore satisfying the criteria that the equipment could be used for a multi-stage process.

The column was then commissioned from a local glassblowing company. The tray for collecting the top product was separated from the column partially due to making the equipment easier to manufacture and also because it would allow for easier cleaning and storage and for ease of access when putting the foam breaker into the column. Four columns were built, two pairs of different heights, but with identical diameters. The diameters selected were smaller than for previous projects. Larger diameters lead to more liquid drainage and therefore reducing the diameter leads to a larger liquid hold up. This was beneficial as the foam would be wetter and therefore the production rate of the top product would be higher. Three cylindrical glass containers were built to hold the feed and products. Glass was used for the columns because surfactants absorb to plastic materials. Using glass therefore meant there would be less discrepancy in a mass balance of surfactant. Glass also allowed for observation of the foam within the column.

The design is shown in Figure 3.3, there are sampling points running along the side of the column and also one at the top. These can be used for either taking foam samples or feeding reflux back into the column.

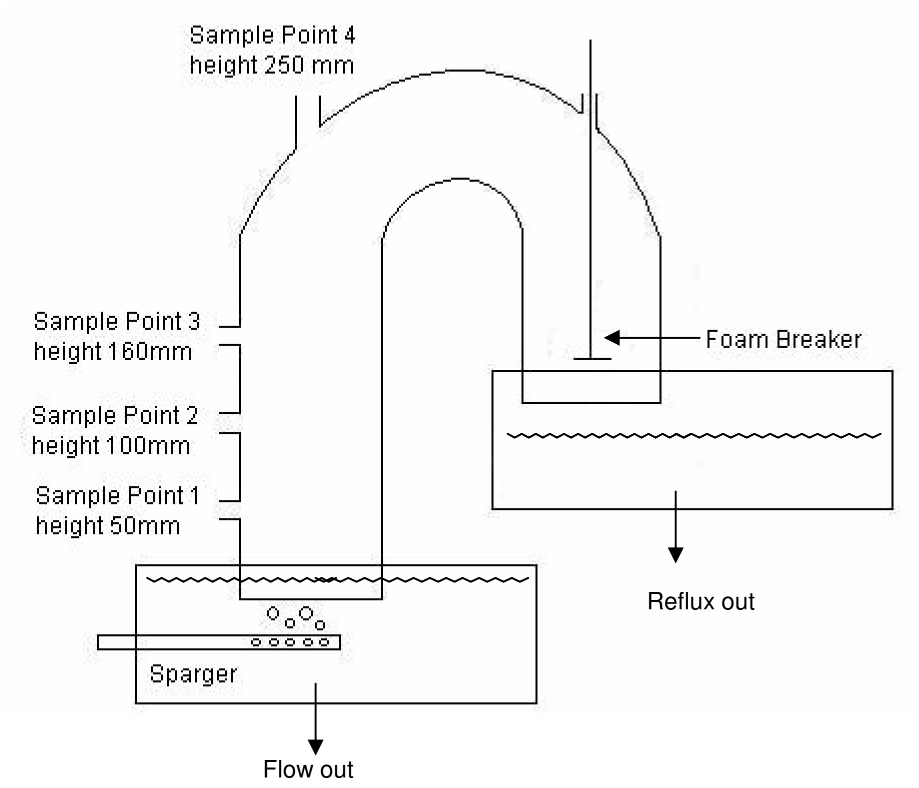

Figure 3.3 Column set-up

3.2 Column, feed and reflux set-up

Only one of the two types of column was used in this project. The shorter column was selected because there would be less liquid drainage and therefore a greater flow rate of top product. A larger flow rate was needed because to use reflux the production rate needed to be greater than the minimum flow rate of the pump; otherwise the reflux would be unsustainable. The column was supported by clamping it to a wall-mounted support to provide stability. The containers for the feed and the top product were placed into rubber bungs with a hole bored into them. The bungs were then clamped. The setup is shown in Figure 3.4.

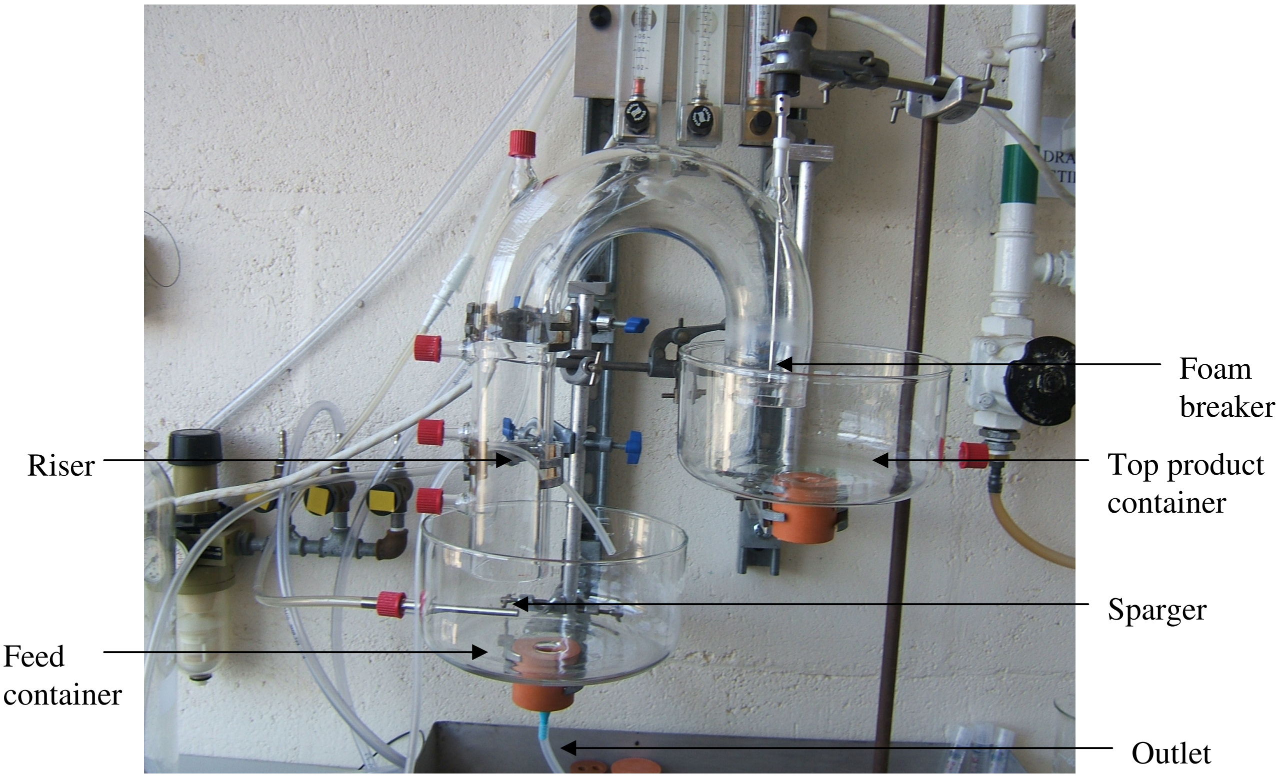

Figure 3.4 Foam fractionation column setup for steady state experiments (no reflux)

The experiments used between 10L to 20L of feed solution. This was originally kept in a plastic container, but the concentration of the feed was found to drop if solution was left overnight. This was almost certainly due to surfactant molecules absorbing onto the plastic. A 20L glass container was used as a replacement and the problem did not reoccur. A pump was used to transfer feed from the reservoir to the container at the bottom of the column. Waste feed was drained from this by simply using a plastic tube which led from the bottom of the container to the sink.

Reflux was taken from the bottom of the top product container and fed back to the column using a Pharmacia Fine Chemicals Peristaltic Pump P1 capable of low flow rates in the range 0.13 ml/min – 12 ml/min for the tubing used (3.1mm diameter).

3.3 Foam Breakage

A mechanical foam breaker was used to break the foam. In previous years an electric drill has been used to rotate the foam breaker. This was essentially over-powered for the application and in addition the drill was very heavy and cumbersome. The electric motor used for the prototype had worked so it was moved onto the actual equipment, and was held in place above the column with a clamp.

The initial foam breaker was a shaft with four paddles at the bottom and was based on previous designs. When this rotated it was found that the foam in the column was blown backwards, the breaker essentially acting as a fan. This was undesirable as it prevented most of the foam reaching the exit point and also affected the way the column ran. Another problem was that when the foam reached the exit the breaker tended to slow and then come to a halt. This was because the motor provided a very high speed, but a low torque.

The problem was resolved by getting a new foam breaker made. Instead of paddles this had thin metal wires, spread radially at the bottom. This removed the problem with the foam being blown within the column. Foam breakage was not entirely satisfactory, with the foam being whipped into a thick secondary foamate rather than breaking. However, this reduced the volume of the foam exiting the column and generally meant that the foam never overflowed the top product container because the rate of foam production balanced with the rate of natural foam breakage. The two foam breakers are shown in Figure 3.5.

A geared electric motor was acquired towards the end of the testing. The intention was that the lower speeds and higher torque provided by this motor would overcome the problems with low torque. However, the foam breakage and production of secondary foamate was reduced leading to greater problems with foam overflowing the container. This was solved by removing foam from the top product container, allowing it to collapse naturally and then returning the liquid left to the top product.

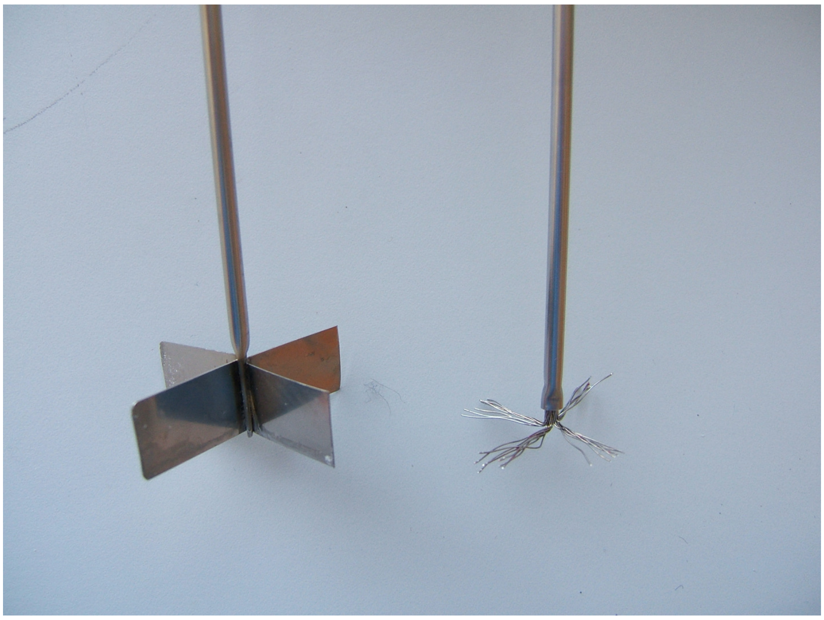

Figure 3.5 Foam breakers

4 Experimental Methods

This section gives details on how measurements were carried out and the difficulties experienced.

4.1 Absorbtion

Cetylpyridinium chloride (CPC) has a well-defined light absorbance peak at 259nm. This can be used to measure the concentration of CPC in solution through the Beer-Lambert law (http://elchem.kaist.ac.kr/vt/chem-ed/spec/beerslaw.htm). The law is that there is a linear relationship at low concentrations between the concentration of an absorbing species in solution and the measured absorbtion.

Using normal deionised water as a baseline a calibration curve for CPC can be measured using the absorbance values at 259nm for solutions of known concentration. An absorbance curve has been produced for CPC in previous 4YPs (Swain 2004, Oyinloye 2005). A new curve was again established for this project to confirm the accuracy of the previous curves.

Each sample was prepared using 500 ml of deionised water. The concentrations measured were from 0 mM to 1 mM, with increments of 0.1 mM. The order the solutions were made up in and measured was randomised. The mass of CPC needed for each solution was measured on a mass balance with an accuracy of +/- 0.0001. After each solution had been made it was stirred for ten minutes with a magnetic stirrer to make sure the concentration was constant throughout the solution. Three measurements were taken for each concentration and the results averaged. The spectrophotometer used was a Heλios Gamma.

4.2 Surface Tension

Section 2.1.1 introduces the concept of surface excess and how it relates to the surface tension of a solution. To calculate the surface excess a Kruss K8 interfacial tensiometer, fitted with a platinum ring was used to measure the surface tension. The solutions made up for the concentration calibration were also used for the surface tension measurements. Three measurements were made for each sample. After measuring the surface tension for each sample the platinum ring was rinsed with distilled water and then dried with a flame to remove any impurities.

4.3 Foam Sampling

Foam sampling was needed to take measurements of the concentration and the liquid hold up in the column. It was done using a method which originated with Swain (2005) and was further developed by Oyinloye (2006).

The method uses a Dymac 14 suction pump, an air flow meter to regulate the rate of suction and a foam sampling device consisting of a sealed test tube with two glass rods penetrating the seal.

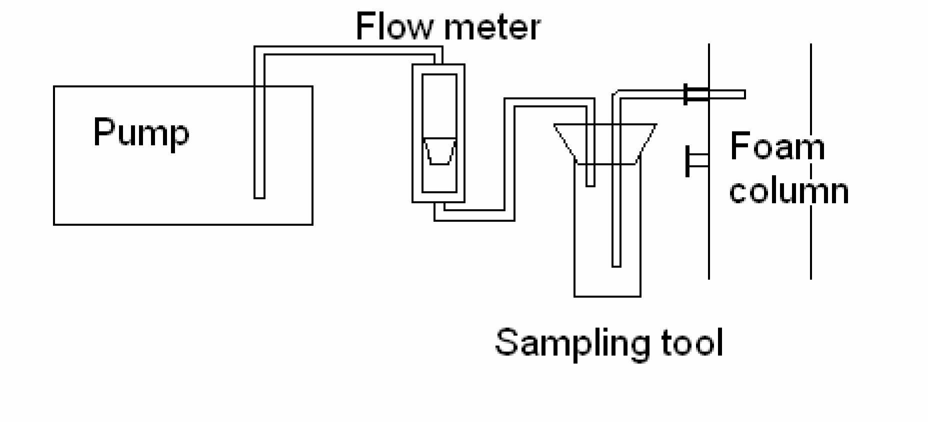

Figure 4.1 Foam sampling set-up

The rate at which foam was sampled could be controlled using the flow meter. A flow rate was found that would extract enough foam over approximately one to three minutes and provide enough liquid to measure the concentration. The flow meter used had a unit scale for which the corresponding air flow rates were not available. The rate of foam extraction was therefore calculated by finding the time it took for the ‘L’ shaped glass rod to fill with foam. Then by using the internal volume of the rod the flow rate could be calculated. The internal volume was found by filling the rod with water ten times and then dividing the amount of water this took by ten. The volume was found to be 1.65 cm^3.

Figure 4.2 Foam Sampling Tool

4.4 Concentration Measurements

Measurements of the feed solution and the top product were done using a pipette to take a sample of the solution. These were then diluted with deionised water to place them in the linear part of the absorbance curve. Foam samples from the column during operation were extracted using the foam sampling tool. The samples were then diluted in the test tubes. All of the solutions sampled were mixed using a magnetic stirrer after dilution.

After mixing the samples were transferred to silica cuvettes and the absorbance measured. Three separate absorbance measurements were taken for each sample and averaged. Following each measurement the cuvettes were rinsed with deionised water.

To calculate the original concentration before dilution the measured concentration was multiplied by the dilution factor, *D*, given by:

$$D = \frac{V_S + V_{LA}}{V_S} \qquad [4.1]$$

V_S is the volume of the sample, V_{LA} the volume of the water added.

4.5 Liquid Hold Up Measurements

Liquid hold up was measured by sampling the foam with the foam sampling tool. It is a measure of the ratio of liquid contained within a particular volume of foam when compared to the total volume of the foam and liquid contained within it and is expressed as

$$\varepsilon = \frac{V_L}{V_f + V_L} \qquad [4.2]$$

The volume of liquid (V_L) was found from the mass of the test tube before and after sampling. All the solutions were assumed to have a density of 1g/ml and therefore the volume of liquid was simply the difference in mass. The volume of foam extracted was calculated from the product of the foam extraction time and the flow rate of foam extraction.

4.6 Foam Column Experiments

There were two types of tests carried out:

1. Steady state tests (with and without reflux)
2. Dispersion tests

The tests were all conducted with the same feed concentration – 1.2 mM. This was because it was above the CMC of CPC. Above the CMC the surface of the solution can be assumed to be saturated with a monolayer of surfactant and have a constant value of surface excess.

The parameters that were changed for the experiments were the gas flow rate being sparged into the feed and the level of reflux. The gas flow rates selected were 1 L/min, 1.5 L/min and 2L/min. 2L/min was the maximum measurable gas flow rate. Higher gas flow rates were desirable because at higher gas flow rates there is a higher liquid hold up and therefore a greater flow rate out of top product. With a greater amount of top product being produced there is more ability to vary the reflux rates.

4.6.1 Feed supply

For steady state the column needs to be operating under continuous conditions. This means that there should be a constant flow in and out of feed solution, with the concentration remaining approximately constant. As the drainage of the feed was done through simply allowing liquid to drain through a tube the flow rate out could only run at one speed. Unfortunately draining the liquid at this speed would mean that a very large feed reservoir was needed. A large enough container for this was not available and there was also not enough CPC to be using it at such a rate.

The solution was to have a semi-continuous feed. During the test for four minutes out of every fifteen the feed was drained and replenished. Measurements of the feed solution showed that the concentration altered at most by approximately 0.01mM. This was still above the CMC and was judged small enough to approximate true steady state conditions.

4.6.2 Steady state tests without reflux

Steady state tests without reflux were the first tests to be carried out. This was to determine how long a column operating under simple conditions would take to reach steady state. This would give an absolute minimum for how long tests could be run for, and when to take measurements that would provide steady state values. The measurements taken also gave a point of comparison for how adding reflux changed the enrichment.

Three steady state tests were carried out, each lasting for two hours. The gas flow rate used was 1 L/min. The lowest gas flow rate was used because previous work has shown that lower gas flow rates take longer to reach steady state. Therefore the time taken for the column running at 1 L/min to reach steady state could be assumed to be the maximum amount of time that would be needed for all the experiment. Foam samples were taken every fifteen minutes from sample point three. The amount of top product produced and the concentration were measured at the end of the tests.

4.6.3 With reflux

Reflux was originally intended to be put into the column at sample point 4. Initial tests to see if the system worked indicated that the reflux was not enriching the top product. To gain an insight into what was happening some qualitative experiments were carried out. These involved injecting or pumping a visual tracer into the column. A CPC solution coloured with red food dye was used for this. From this it was possible to see how the solution spread out into the foam.

Tests with reflux were carried out with reflux entering the column through sample point 3 through a metal sparger. Tests originally ran for two hours and then extended to three for reasons that will be explained in Section 5.3. Foam samples were taken every fifteen minutes. Sample point 4 was sampled twice as often as the other two points. This was to aid in identifying steady state. Table 4.1 shows a typical sampling pattern:

Time	Foam sampled from
15	1
30	4
45	2
60	4
75	1
90	4
105	2
120	4

Table 4.1 Order of Samples

True reflux would be established by running the column without reflux until some top product was generated. Reflux would then begin, and the concentration of the top product would slowly increase until equilibrium was reached. Due to time and material constraints the liquid used for reflux was made up before the test.

To work out the concentration that was needed a trial and error approach was used. This involved feeding a solution of certain concentration to the column as reflux and then measuring the top product concentration. If this was the same concentration as the reflux then it was the correct concentration to use. For the actual tests 100 ml of the correct concentration solution was put in the top product container and fed back as reflux from the start of the test.

4.6.4 Dispersion (Tracer) Experiments

4.6.4.1 Conductivity Probes

By measuring conductivity a value for the dispersion coefficient could be found. Three different methods of measuring conductivity were tried, each meeting with differing degrees of success. All involved having conductivity probes running from the column to Digitek INO 2513 multimeters measuring resistance. The readings from the multimeters were then logged by a computer using Digitek data logging software. The resistance measurements were converted to conductivity by inverting them.

A number of different types of probes were tried for measuring conductivity. The best method was to simply insert two stripped wires through each sample point. By putting a small amount of blu-tac opposite the sample point the ends of the wires could be pushed into it and kept in position. The resistance between the two wires was then logged. This worked and provided very consistent measurements. The major problem was that it was hard to make the gap between the wires consistent between each sample point. This was because the wires were flexible and it was not possible to get them perfectly parallel to each other. The method could be improved by using thin rigid metal rods instead of wires, but time constraints meant there was not time to acquire these.

The main problem with this method was that with the wires inserted through the sample points it was not possible to log the resistance during steady state tests to see how conductivity changes over the test and if it reaches a steady value. However, it did mean that measurements could be taken for dispersion experiments.

4.6.4.2 Conductivity Measurements

Using the simple wire probes to take measurements probes were inserted through sample point 2 and sample point 3. The resistance was then logged by a computer. Once steady readings are obtained injecting a salt solution into the column allows a measurement of dispersion. This is because the salt acts like a tracer, increasing the conductivity. By recording the change in conductivity as the tracer moves through the column a value for the dispersion coefficient can be calculated.

Section 2.2.1 describes how dispersion coefficients can be calculated from a concentration curve of a tracer injected into a column. A salt tracer was introduced to the column and concentration curves were obtained.

4.6.4.3 Method

The column was run without reflux for approximately ten minutes. When it was clear that the values being logged were stable a salt solution was injected into sample point 1. The salt solution was injected using a plastic syringe and contained 0.5 ml of salt solution. Concentration of the salt solution was approximately 1 g/L. Injection took place over 2 seconds, this was slow enough to stop the sudden inrush of liquid from disturbing the foam, but fast enough to come close to an instantaneous injection. The data was logged until the measured values returned to approximately the values before injection. The resistance was sampled at 1 Hz.

5 Experimental Results and Discussion

This section will outline the results of the experiments and will discuss the findings.

5.1 Concentration Calibration

Figure 5.1 shows the average absorbtion values at 259 nm against concentration for CPC.

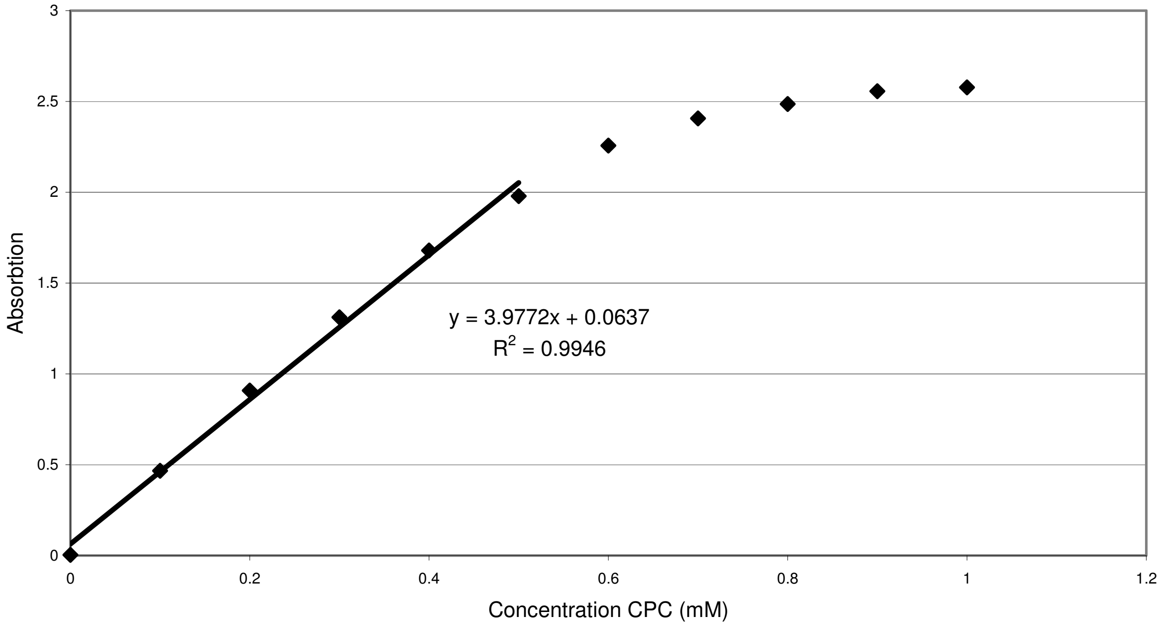

Figure 5.1 Absorbance curve for CPC at 259 nm

The relationship was taken to be linear for absorbtion values below 2, which corresponds to a concentration of approximately 0.5 mM. The equation used to calculate the concentration is shown on Figure 5.1.

5.2 Surface Tension and Surface Excess

Figure 5.2 shows the values of surface tension measured plotted against $\log_{10}$ of the concentration solution. Figure 5.3 shows the results of a similar experiment by Aubourg *et al* (2000). Figure 5.3 was used by previous 4th year projects to calculate values of surface excess.

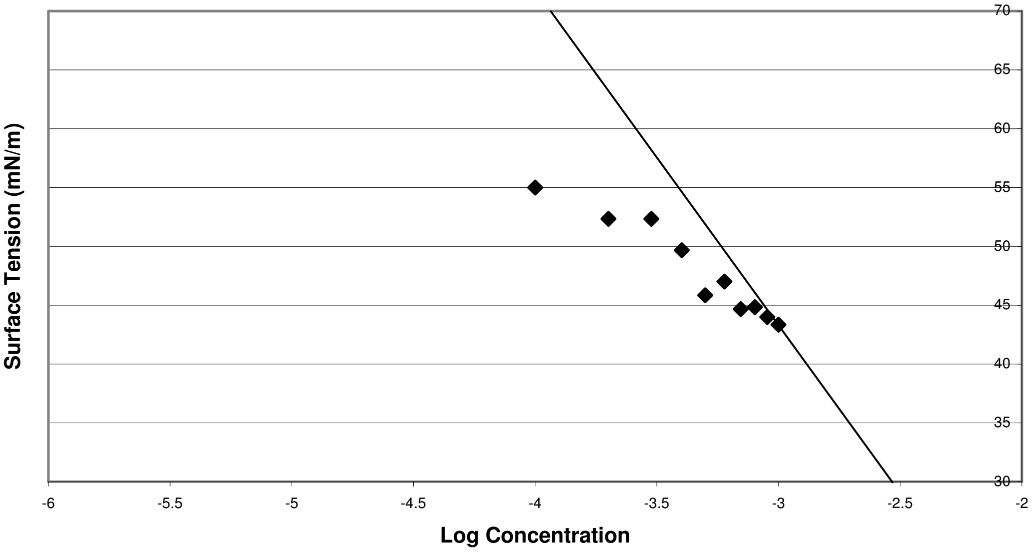

Figure 5.2 The effect of increasing CPC concentration on surface tension

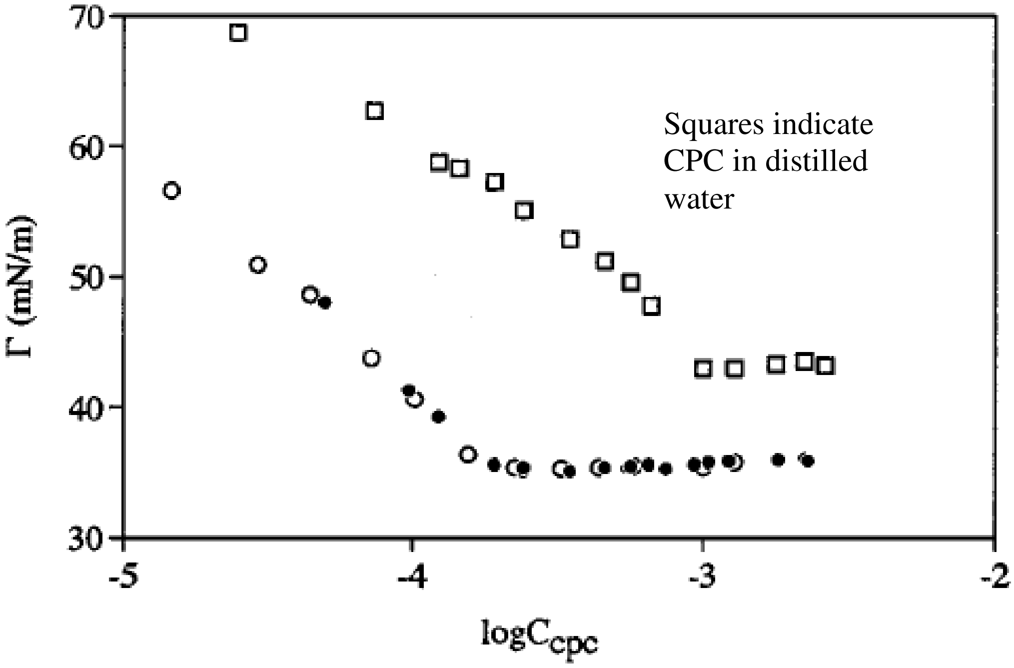

Figure 5.3 Variation of surface tension with CPC (Aubourg et al 2000)

5.2.1 Discussion

Equation 2.2 indicates that the surface excess can be calculated by considering the variation of surface tension against concentration.

By taking the maximum change in surface tension the maximum value of surface excess can be found. Using the values from Figure 5.2

$$\frac{d\gamma}{d\ln C} = \frac{d\gamma}{\ln(10^{\log C})} = \frac{14.5\times10^{-3}}{\ln\left(10^{-0.5}\right)} = \frac{14.5\times10^{-3}}{-1.15} = -12.61\times10^{-3} \qquad [5.1]$$

This value can then be substituted into equation 2.2 to obtain a value for the maximum surface excess.

$$\Gamma_\infty = \frac{1}{nRT}\frac{d\gamma}{d\ln C} = \frac{-12.61\times10^{-3}}{2\times8.314\times298} \qquad [5.2]$$

$$\Gamma_\infty = 2.54\times10^{-6}\,mol/m^2 \qquad [5.3]$$

This compares favourably to the value calculated from Figure 5.3, which is $2.64\times10^{-6}\,\mathrm{mol/m^2}$. A value of 2.6 x 10^{-6} will be used for the value of maximum surface excess.

5.3 Steady State Without Reflux

Figure 5.4 and 5.5 show the results for all three tests for concentration and liquid hold up. Figure 5.7 shows the average values for the three tests. The two outliers shown in Figure 5.5 – one at 115 minutes and one at 120 minutes have not been included in the averages.

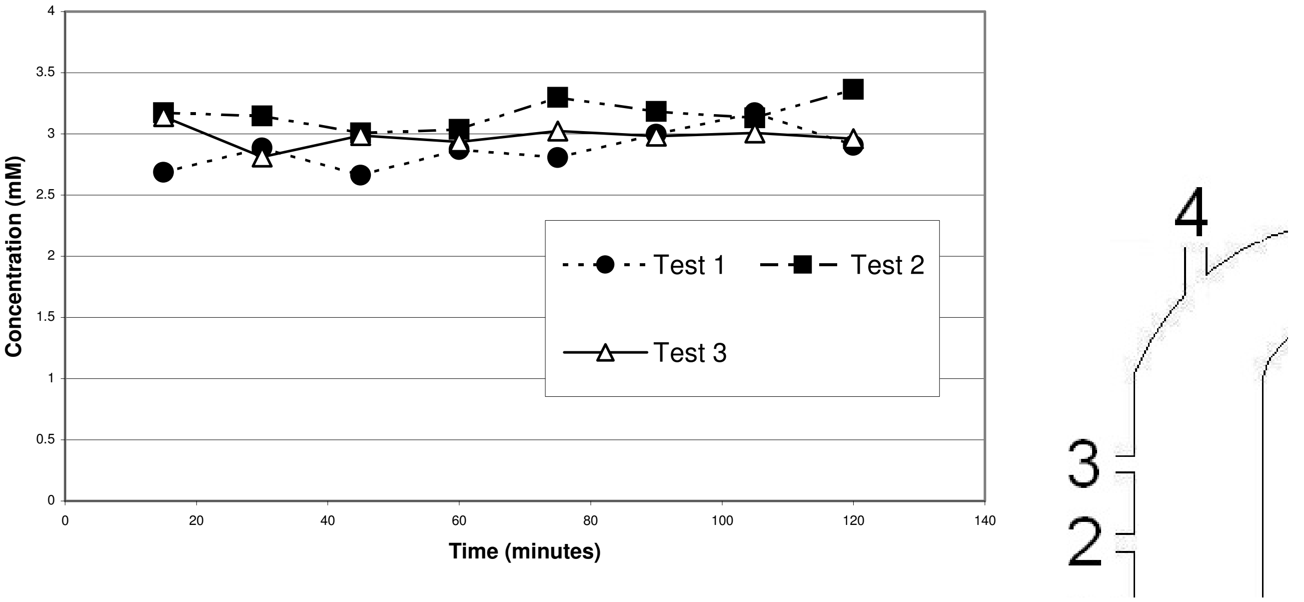

Figure 5.4 Sample point 3 concentration, gas flow rate 1L/min

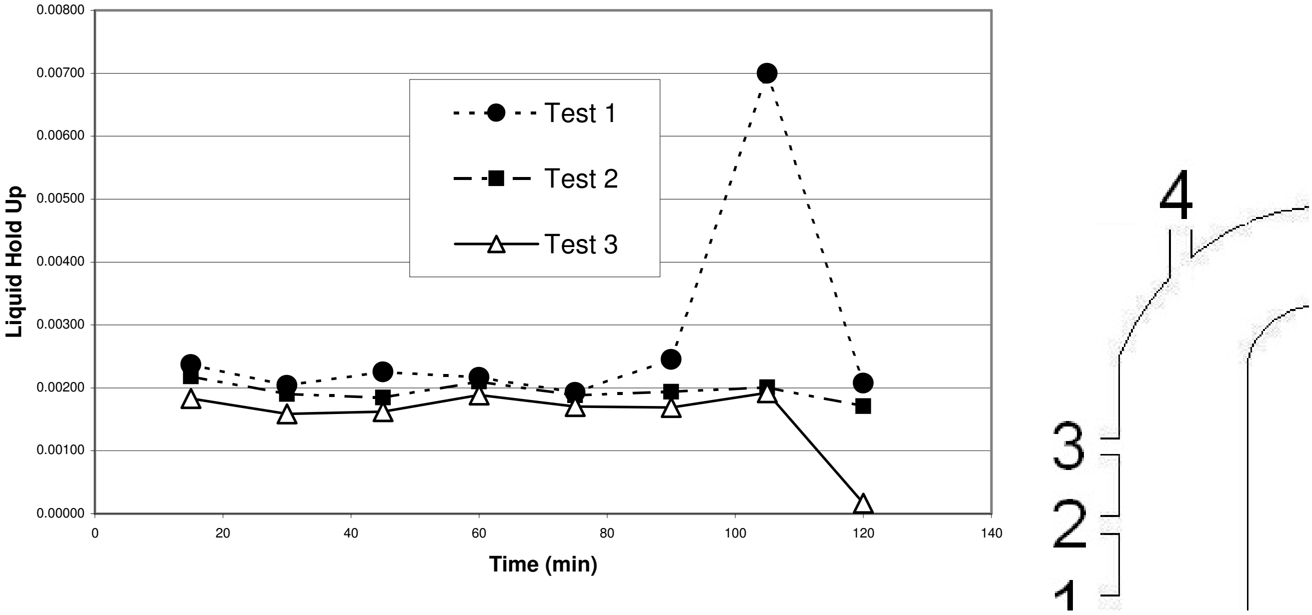

Figure 5.5 Sample point 3 liquid hold up

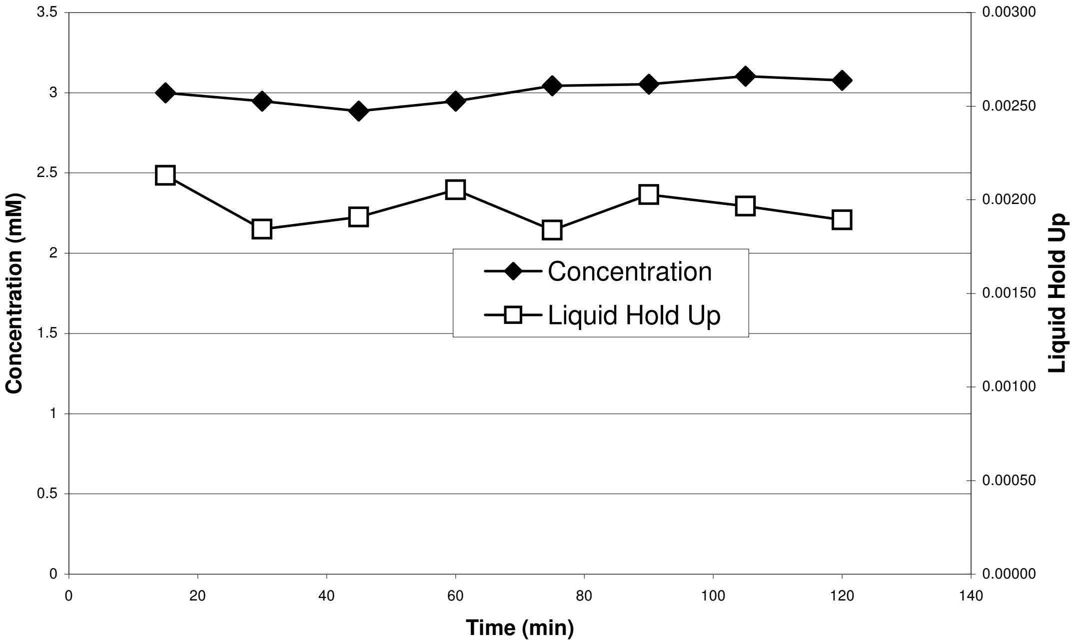

Figure 5.6 Average values of concentration and liquid hold up

Two tests, one at 1.5 L/min and one at 2 L/min were also carried out to get values for the top product concentration and production rate. Table 5.1 shows a comparison of the values obtained for each gas flow rate.

	1 L/min	1.5 L/min	2 L/min
Concentration (mM)	9.78	6.82	4.87
Enrichment	8.15	5.68	4.06
Rate of production (ml/min)	0.36	0.8	1.23

Table 5.1 Comparison of top product values for different gas flow rates (no reflux)

5.3.1 Discussion

The results for the steady state tests without reflux were mainly consistent. The concentrations fluctuate, which is most likely due to the dynamic nature of the system. Some of the fluctuation is also likely to be down to experimental error caused by the tolerance of the mass balance and pipettes used.

The outliers on Figure 5.5 are probably due to two different factors. The outlier on test 1 at 115 minutes shows a much greater liquid hold up. This may be due to some liquid being left on the test tube after cleaning therefore altering the total mass or it could be because the mass balance was disturbed and needed re-zeroing. The outlier in test 2 where the liquid hold up is much less could be because of a problem with the suction pump. If there was an air leak somewhere in the connections the pump may not have pulled as much foam out of the column.

From the results it was seen that the column seemed to have reached a steady state by the time of the first measurement at 15 minutes. The repeatability of the results was good with the maximum difference between the measured concentration values being 0.7 mM. In comparison steady state measurements by Oyinloye (2006) had a maximum difference of approximately 13 mM over approximately the same time scale. However, Oyinloye’s column was running with the foam breakage taking place within the top of the column, and all the foamate running back into the rising foam. This is total reflux and one possibility for the difference is that the refluxing column had not reached steady state.

5.4 Steady State With Reflux

5.4.1 Visual Tracer Results

Figures 5.7 – 5.9 show how the dye moved through the column for a variety of conditions. Each set of photos were taken over approximately 30 seconds.

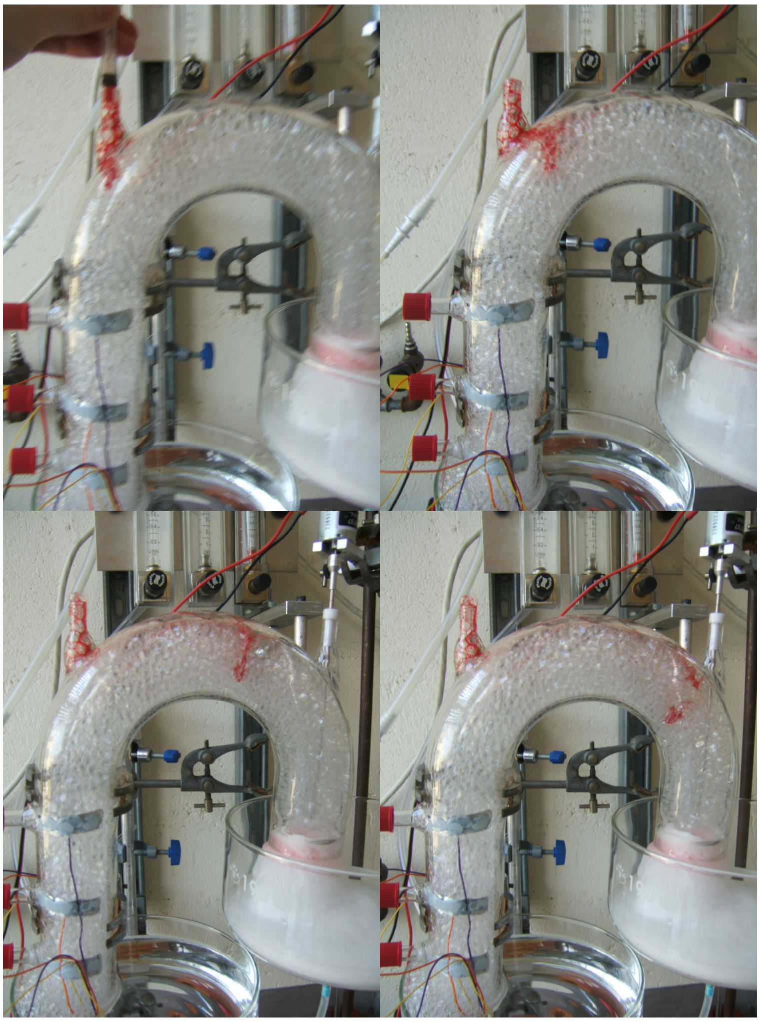

Figure 5.7 Injection of food coloured solution. 2L/min gas flow

In Figure 5.7 it can be seen that the injected liquid moves over the top, rather than running back down through the rising vertical column of foam. As it can be assumed that the majority of the enrichment occurs through the vertical section this explains why in the initial tests reflux did not have an effect. For the other gas flow rates the results were similar, but the red solution spread out more as it moved along the curve instead of remaining concentrated along a line as in Figure 5.7.

Figure 5.8 shows the results when the dye was pumped into the column. It was harder to get visual results as the rate of solution entering the column was much slower. For this reason the dye was pumped at a much greater rate than would be sustainable for normal reflux. The pictures show that the distribution of solution through the foam is greater if it is pumped rather than injected. However a significant amount still goes straight over the top and the solution can also be seen to accumulate along the sides of the inner bend of the column.

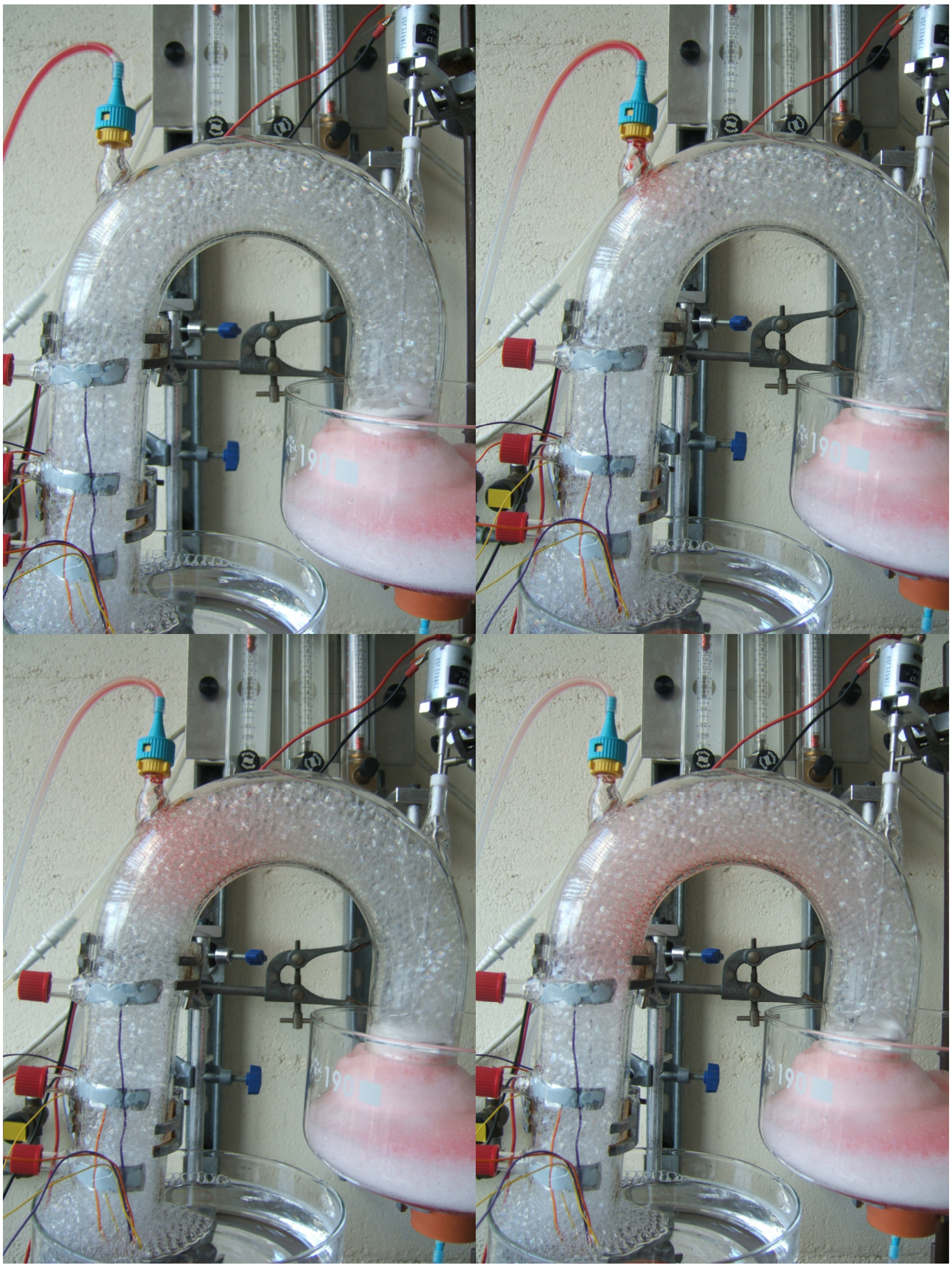

Figure 5.8 Food dye pumped at 12.3 ml/min. Gas flow rate 2L/min

To try and achieve a better flow of reflux through the foam the reflux entry point was moved to sample point 3. To stop the flow draining down the sides of the column the reflux was pumped through a stainless steel manifold spanning the column width, with the holes positioned in the centre of the column. Figure 5.9 shows how this improved the flow of reflux through the column.

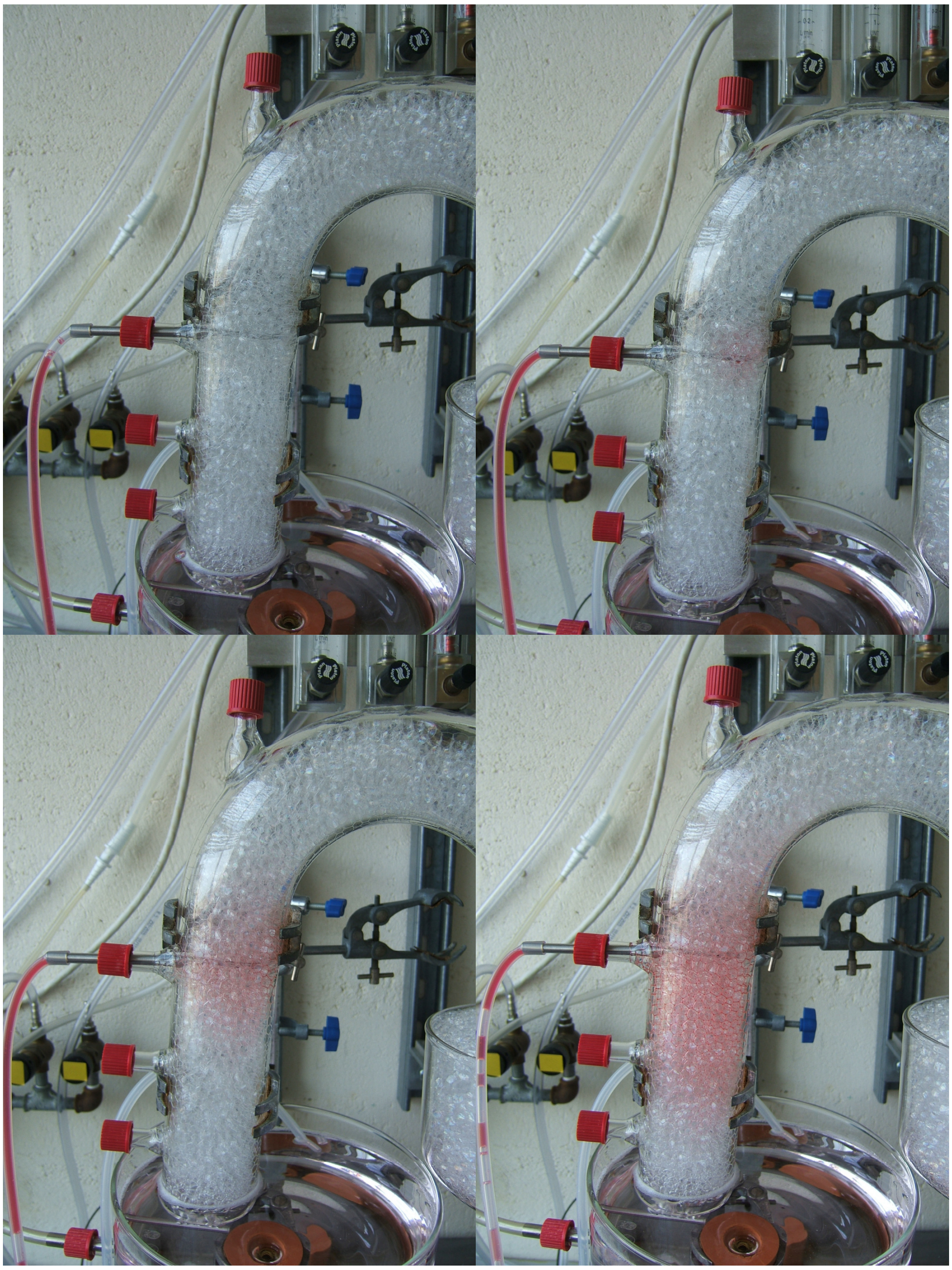

Figure 5.9 Food dye pumped at 1.23ml/min through a metal sparger. Gas flow rate 2 L/min

5.4.2 Quantitative Results

Achieving repeatable results with reflux was more difficult than with the tests without it. Refluxing columns take longer to reach steady state (Lemlich 1972), and it was anticipated that this might cause some difficulties. Without reflux the column took approximately fifteen minutes to reach steady state. It was therefore initially decided that two hours should be enough time to reach steady state and take measurements. Over the first few tests at 1 L/min it became apparent that consistent results were not being achieved. A six hour test was therefore carried out to try and determine if steady state with reflux could be obtained in the time available for testing.

Figure 5.10 shows the results of the six hour test. Vertical bars showing the maximum and minimum possible values for each data point based upon experimental error are shown. Appendix C shows how the experimental error was calculated. From the results it can be seen that steady state appears to be reached for sample points 1 and 4, relatively quickly. There is however a possible trend towards an increase in the concentration at sample point 4 after 180 minutes.

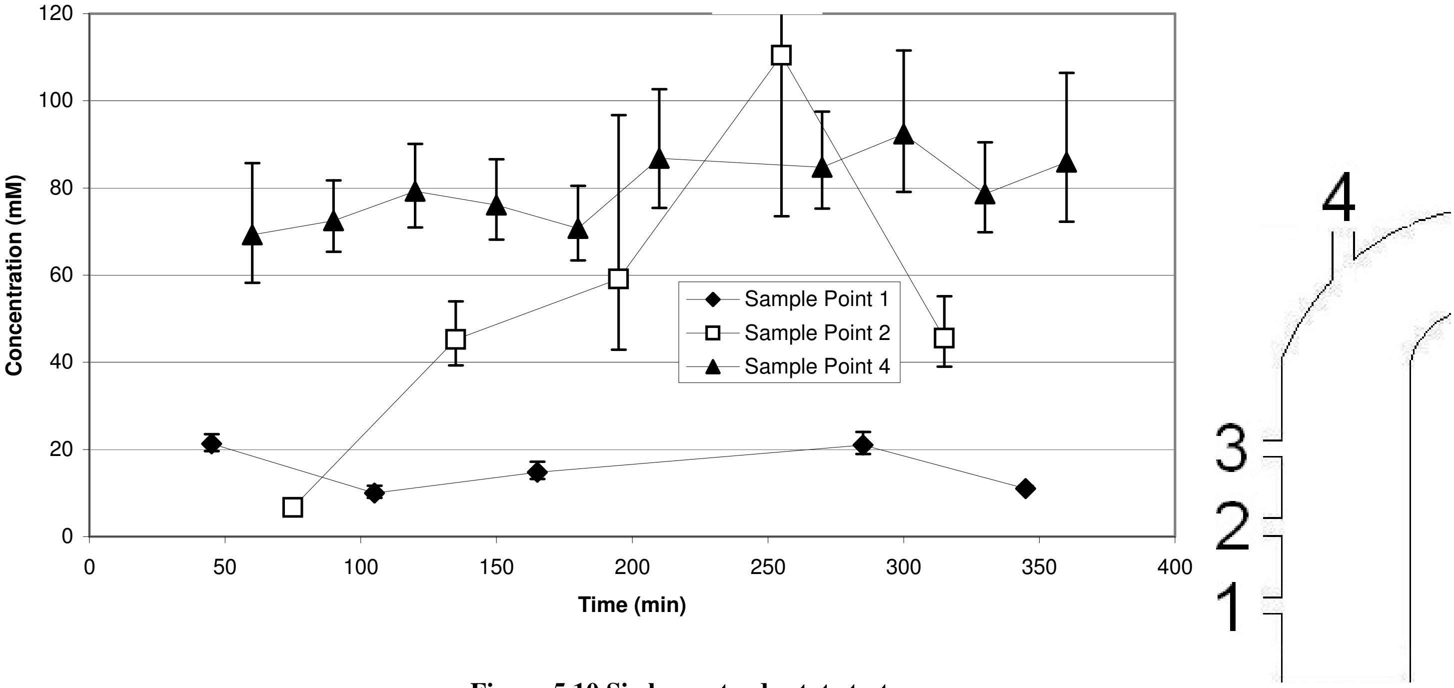

Figure 5.10 Six hour steady state test

The data point at 255 minutes for sample point 2 appears may be an outlier, which means that steady state occurs at around 120 minutes at sample point 2.

From this data it was decided that steady state tests should be carried out for three hours, with the values measured between 120 minutes and 180 minutes taken as being steady state. This was because the values appeared relatively steady after 120 minutes and also due to constraints on the time available to carry out tests.

Results were obtained for two tests for 1L/min, three tests for 1.5L/min and one test at 2L/min. The results for the 2L/min test showed reflux to be having very little effect on enrichment and there was not time to investigate this further. Using reflux altered the production rate of top product (both flow out and flow for reflux) so it was not possible in the timescale to get a set of results for exactly the same reflux ratios though it was attempted for 1.5 L/min and 2 L/min. The reflux ratios were

- Total reflux – 1 L/min
- 0.286 – 1.5 L/min
- 0.152 – 2 L/min

Figures 5.11 and 5.12 show the liquid hold up and concentration profiles measured.

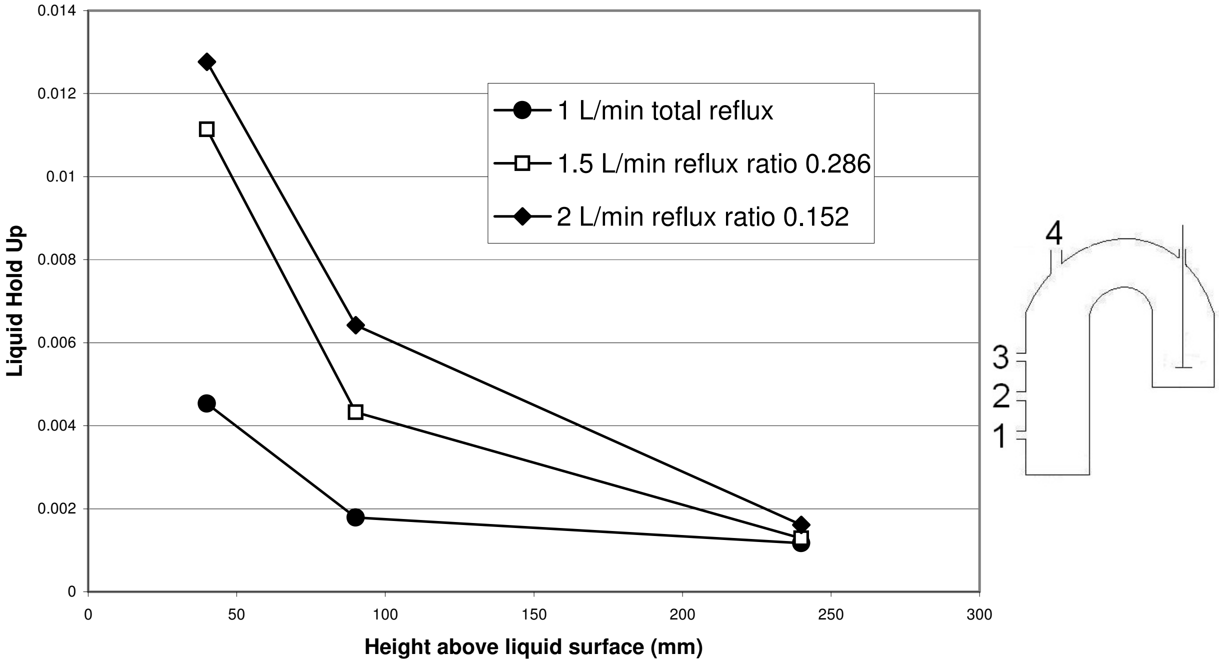

Figure 5.11 Average liquid hold up over column

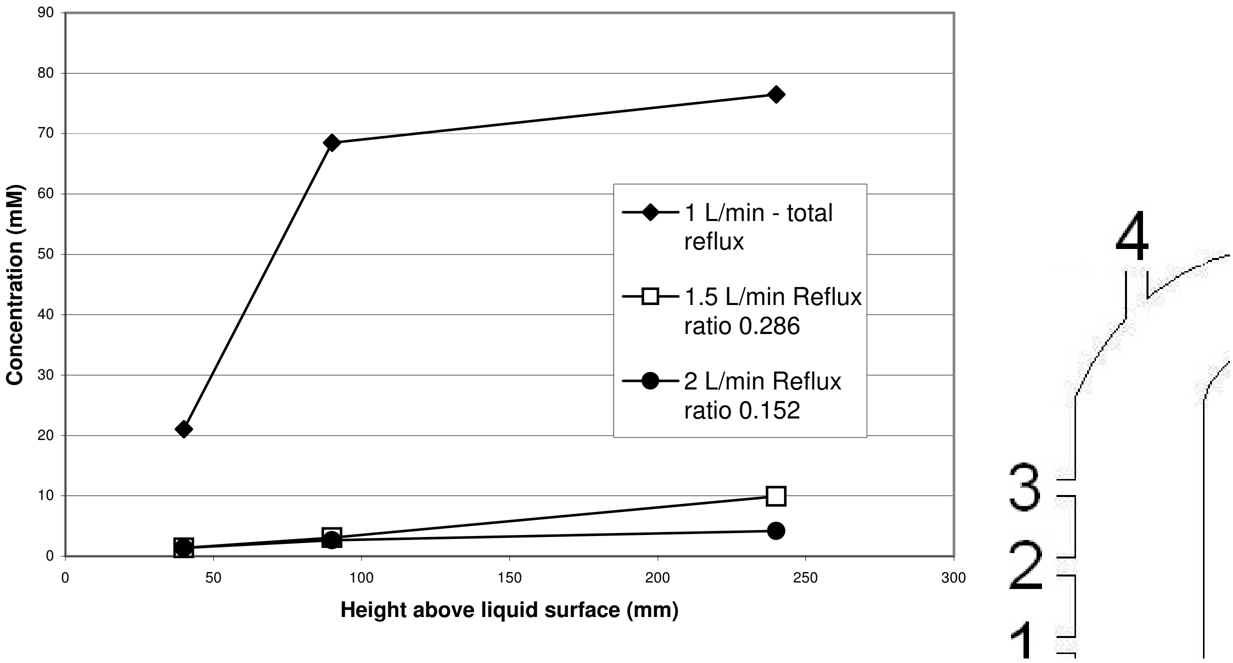

Figure 5.12 Average concentration over column

The top product concentrations and enrichment for each flow rate are shown in Table 5.2.

	1 L/min	1.5 L/min	2 L/min
Concentration (mM)	63.64	11.12	4.92
Enrichment	53.03	9.27	4.1

Table 5.2 Top product concentration and enrichment for steady state tests with reflux

5.4.3 Discussion

Figure 5.11 shows decreasing liquid hold up as the height of the column increases. It is notable that the liquid hold up is greatly increased lower down the column for increased gas flow rates. Higher up the column at 240 mm the liquid hold up values are much closer. As the liquid hold up becomes approximately constant higher up a column this suggests that for a taller column the liquid hold ups at different gas flow rates may tend towards similar values.

Figure 5.12 shows increasing concentration with increasing column height. It also strongly demonstrates the enriching effect of reflux. With total reflux at 1 L/min the concentration at sample point 3 is over six times that of the concentration for 1.5 L/min with a reflux ratio of 0.286.

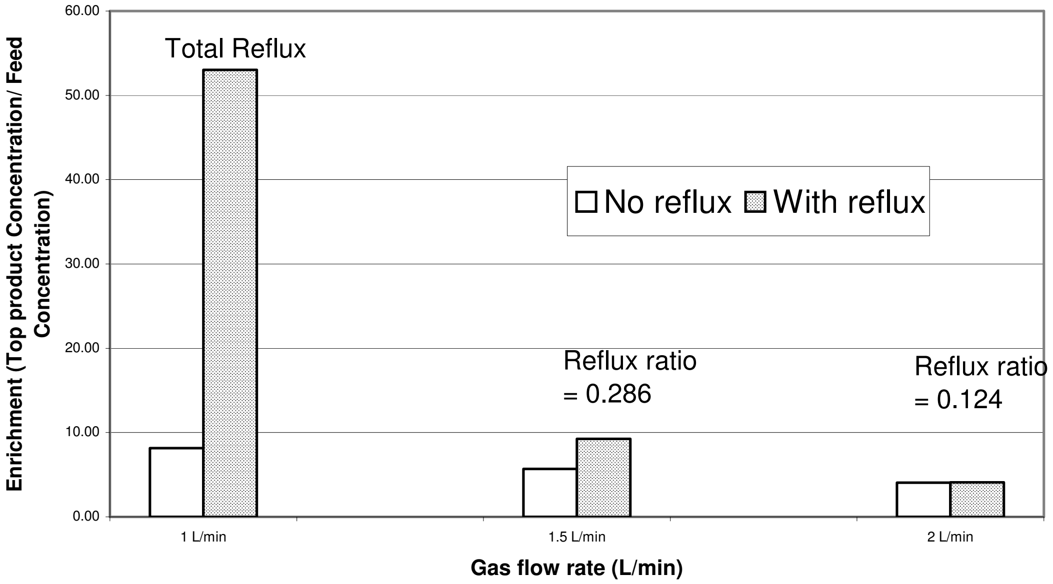

Figure 5.13 Comparison of enrichment ratios with and without reflux

Figure 5.13 shows a comparison of the enrichment between the experiments with reflux and without. It demonstrates how increasing the reflux ratio can have a dramatic effect upon enrichment; with total reflux at a gas flow rate of 1 L/min the enrichment is 6.5 times greater than with no reflux. At 1.5 L/min with a much smaller reflux ratio the increase in enrichment is more modest, but still has a significant increase.

The enrichment with reflux for 2 L/min has a negligible increase compared to enrichment with no reflux. This may be due to the reflux not cascading down the column in sufficient quantities, with the majority of the reflux going up the column. While the qualitative analysis indicated that the reflux was distributing well the flow of dye was much faster than was actually used during real reflux. This was because it was difficult to see the food dye at low flow rates, but may mean that the distribution was not as positive as it appeared. Repeat experiments with the reflux being put in even lower down the column would help establish if this was the problem.

It was intended to calculate the number of equilibrium stages in the column. However, it was not possible to calculate the flow rate up of interstitial liquid so an equilibrium line could not be drawn for the graphical method. It was also not possible to use

Stevenson *et a*l's (2006) empirical approach as the constants needed were not known. If forced drainage experiments were carried out for this column the number of equilibrium stages could then be calculated.

5.5 **Dispersion**

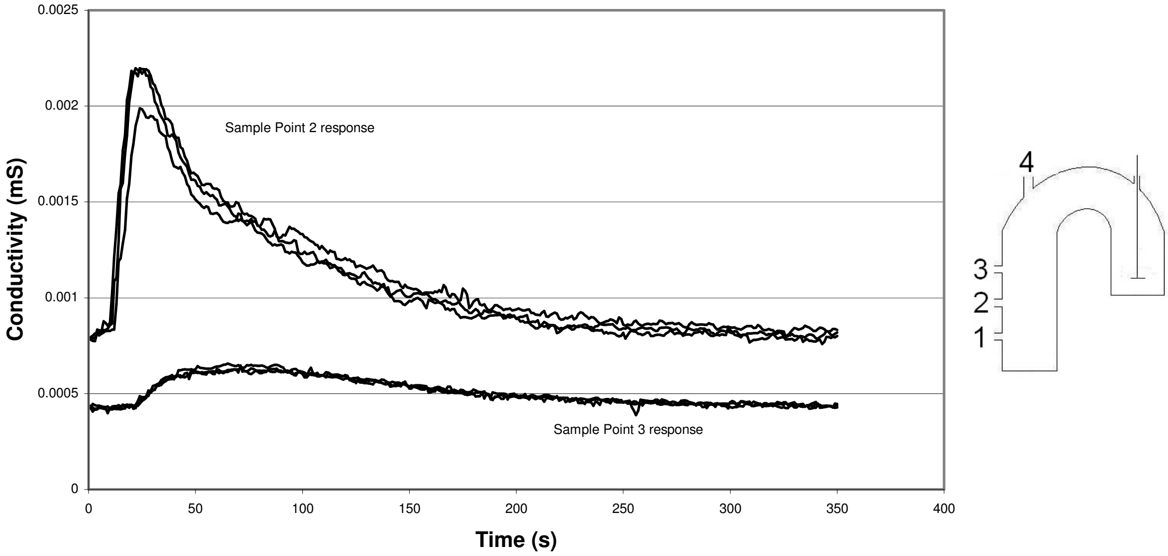

Figure 5.14 Conductivity response at 1L/min gas flow rate

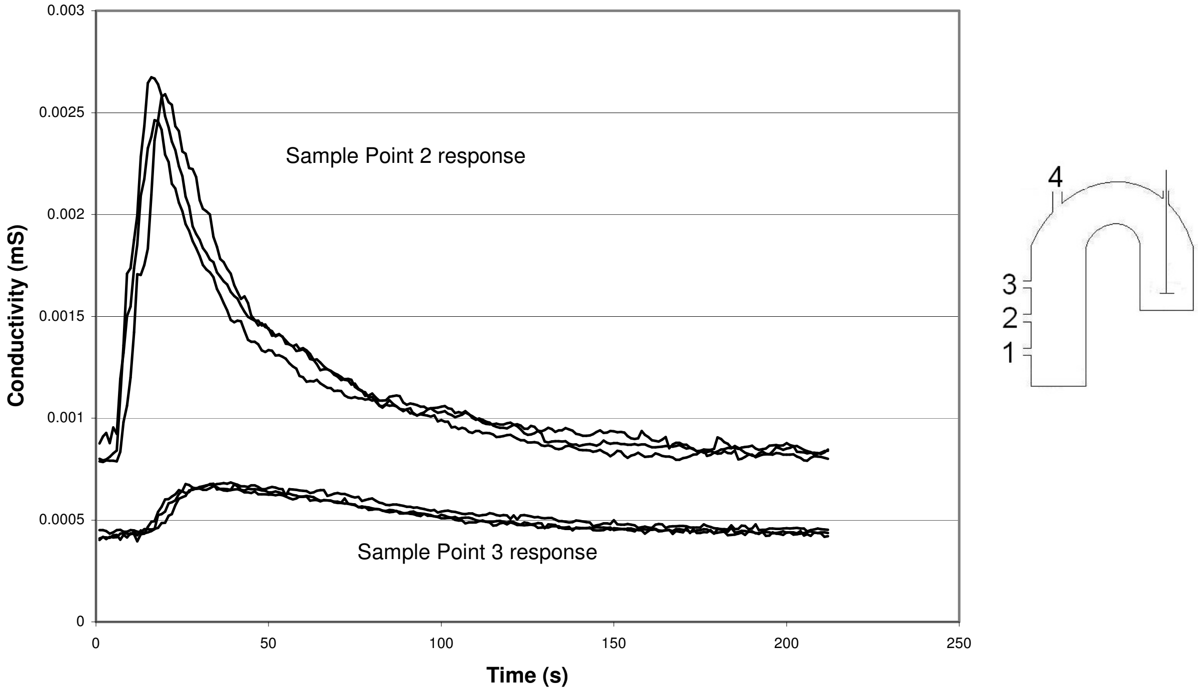

Figure 5.15 Conductivity response at 1.5 L/min gas flow rate

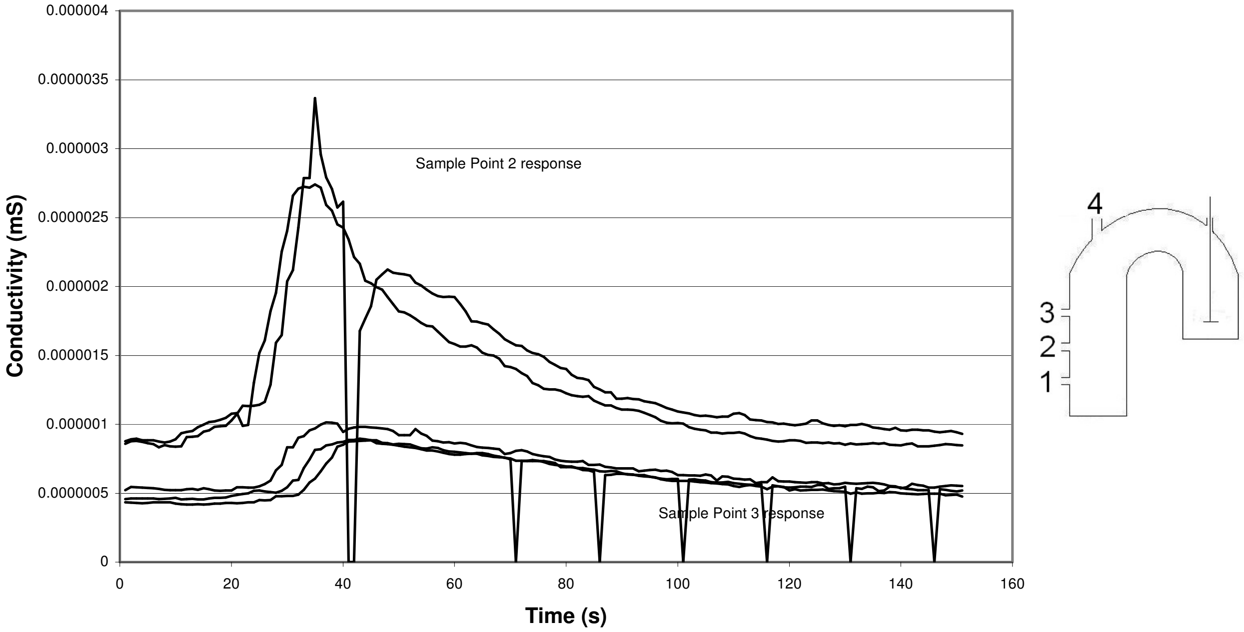

Figure 5.16 Conductivity response at 2 L/min gas flow rate

Figures 5.14 and 5.15 show the response for three tests run at 1 L/min and 1.5 L/min. The set of sharper peaks is the response at sample point 2, immediately above the injection point. The flatter broader response is at sample point 3. The results were very repeatable. Figure 5.16 shows the results for 2 L/min. For this air flow rate two test results were recorded for sample point 2 due to problems with the data logger. The 2 L/min tests were more problematic with a sudden drop in the sample point 2 measurement for one of the tests and spikes in one of the sample point 3 measurements. The spike in sample point 2's data may be due to bursting of the foam bubbles and coalescence leading to there being no path for conduction between the probes. For sample point 3 the problem appeared to be with the data logger.

5.5.1 Discussion

By recording the conductivity curves as the tracer passes the probes the dispersion coefficients can be calculated as outlined in Section 2.2.1. The curves have characteristics such as the variance and these can be calculated through the recorded discrete data.

The variance is given by

$$\sigma^2 = \frac{\int_0^\infty t^2 C dt}{\int_0^\infty C dt} - t^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \qquad [6.1]$$

where $\bar{t}$ is

$$\bar{t} = \frac{\int_0^\infty t C dt}{\int_0^\infty C dt} = \frac{\sum t_i C_i \Delta ti}{\sum C_i \Delta t_i} \qquad [6.2]$$

The variance has units of time^2 and as such can be made dimensionless by

$$\sigma_\theta^2 = \frac{\sigma^2}{(\bar{t})^2} \qquad [6.3]$$

Once the numerical value of the dimensionless variance is calculated it can be equated to the dimensionless dispersion coefficient using Equation 2.13. An example of these calculations is in Appendix D. Table 5.3 shows the calculated values for each gas flow rate

Dimensionless Dispersion coefficients (D/uL)				
1 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.177471	0.169763	0.158433	**0.168556**
Sample Point 3	0.119773	0.123731	0.122804	**0.122103**

1.5 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.1716	0.1872	0.1951	**0.184651**
Sample Point 3	0.1184	0.1263	0.1265	**0.12376**

2 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.0748	0.0852	NA	**0.079974**
Sample Point 3	0.0838	0.0702	0.0954	**0.083128**

Table 5.3 Dimensionless dispersion coefficients

To calculate the dispersion coefficients the values of the superficial gas velocity, *u*, and the height of the sample point above the liquid pool are needed. The height is a simple measurement (Sample point 2 was 90mm above the pool, sample point 3 150mm). The superficial gas velocity is calculated using the measured value for liquid hold up

$$u = \frac{G\varepsilon}{A} \qquad [6.4]$$

where A is the column's cross Sectional area and G is the gas flow rate.

Dispersion coefficients (mm^2/s)				
1 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.209016	0.199938	0.186594	**0.198516**
Sample Point 3	0.207569	0.214428	0.212823	**0.211606**

1.5 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.3940	0.4536	0.4478	**0.431782**
Sample Point 3	0.3710	0.3958	0.3963	**0.387697**

2 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.2549	0.2902	NA	**0.272518**
Sample Point 3	0.2743	0.2299	0.3124	**0.272205**

Table 5.4 Dispersion coefficients

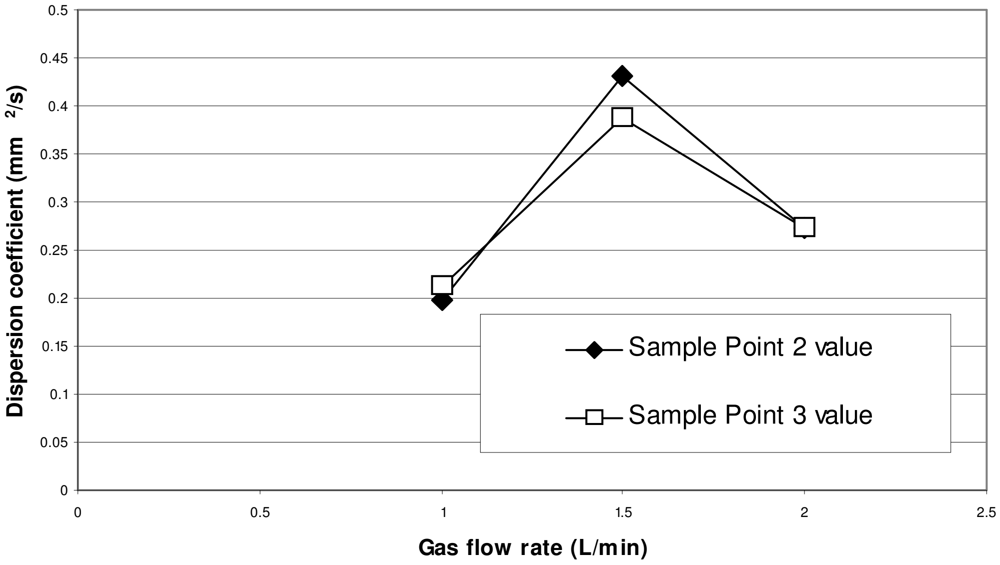

Figure 5.17 Dispersion coefficients at different gas flow rates

The values of the dispersion coefficients for each gas flow rate were very repeatable between tests and sample points. However, the relationship between the dispersion coefficient and increasing gas flow rate was not as expected. Swain (2005) found that between 0.4 L/min and 0.7 L/min the dispersion coefficient increased with the rate of increase becoming greater as the flow rate increased. Figure 5.16 shows that with this equipment the dispersion coefficient increased between 1 L/min and 1.5 L/min and then dropped at 2 L/min.

The 2 L/min data had unexpected spikes in it, suggesting there may have been something wrong with the measurements during the test. However, the data without spikes produced a similar value for the dispersion coefficient so this can most likely be discounted. The tracer also took longer to produce a large increase in the conductivity than for the 1 L/min and 1.5 L/min tests, with there being a slower increase at first. This is unexpected, as with the greater gas flow rate it would be expected that the tracer would reach the higher sample points sooner.

One possibility is that because the tracer injection should be instantaneous but is in fact over a couple of seconds the higher gas flow rate leads to a separation of the tracer as it is injected. Assuming that this is the case then the initial slow rise in conductivity could be discounted as a false response.

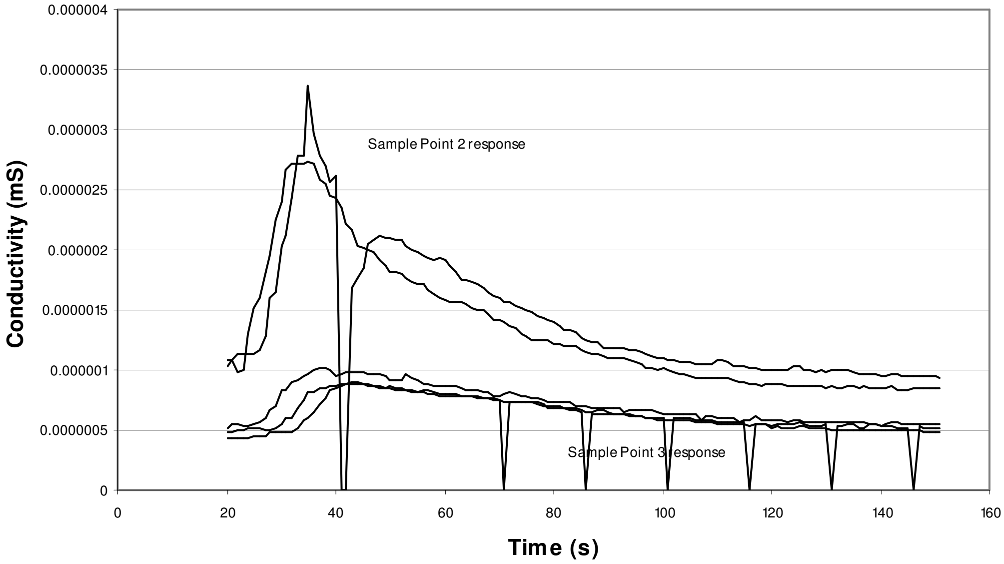

Figure 5.18 Modified 2L/min curve, removing early response

Removing this data (see fig 5.18 for what has been discounted) and recalculating the dispersion coefficients the new values are:

Dispersion coefficient (mm^2/s)				
2 L/min	Test 1	Test 2	Test 3	**Average**
Sample Point 2	0.4772	0.2796	NA	**0.378381**
Sample Point 3	0.3864	0.3430	0.4199	**0.38311**

Table 5.5 Alternative dispersion coefficients

Test 2 still shows a similar value for sample point 2, but this is the test where there is a sudden drop in the curve, which takes a few seconds to recover. While the dispersion coefficient values are still less than the result for 1.5 L/min they are increased. This suggests that it is a problem with the injection of tracer taking place over too long a time. In a repeat experiment a way to remedy this could be to inject a smaller volume of tracer so that the injection could be faster.

6 Application to Novel Biosurfactant Broth

One potential application of foam fractionation is for the separation of biosurfactants. Biosurfactants are produced by microbes, typically in low concentrations, from which they cost a lot to separate.

There is currently collaborative work between the University of Oxford and Oxford Brookes University on producing surfactin. Surfactin is a powerful biosurfactant. The opportunity arose to try and concentrate a surfactin solution that had been produced through this work. This was valuable to this project as a ‘proof of concept,’ although it does not deliver insight into the performance of the column.

6.1 Method

The column was to initially run without reflux, and then, as a top product was collected, reflux would be introduced. The column ran in a batch mode as there was only approximately 2L of surfactin solution. The flow rate of top product was measured by holding the top product container with a stand resting on a mass balance.

The concentration of surfactant in the feed and top product was measured using a surface tensiometer. Measurements of the samples absorbtion spectrum were also taken with a view to identifying any increase in absorbtion at a particular wavelength after enrichment.

The air flow was originally set at 2 L/min, however this was completely inadequate, with the foam only just reaching above the first sample point. A new air flow meter with a much greater capacity was then used and the air flow rate set at 20 L/min.

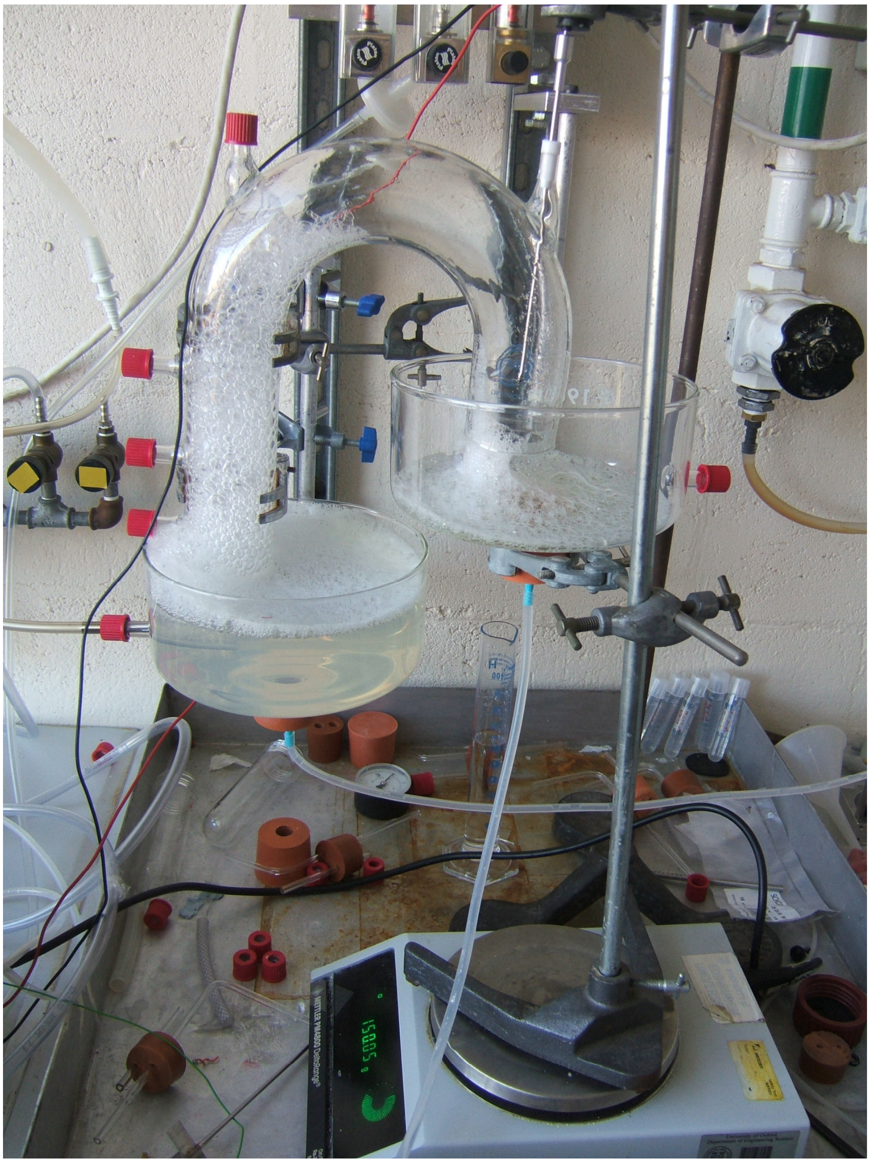

Figure 6.1 Surfactin experiment

6.2 Results

6.2.1 Qualitative

The operation of the column was very different to that when using the lower air flow rates. The foam moved up the column in surges, with the right hand portion of the column being clear of foam, as any which was pushed into it ran rapidly into the top product container. The test also ran a lot more quickly. With the batch operation after fifteen minutes the feed was depleted to the point that there was no solution exiting as a top product. When reflux was started the foam began to reach over the top again. This showed that the reflux was stabilising the foam.

6.2.2 Quantitative

Sample	Dilution Factor	Measured Surface Tension
Feed (before test)	6.24	52
Feed (after test)	5	54
Top product (before reflux)	9.22	44.5
Top product (after reflux)	11.13	50.5

Table 6.1 Measured surface tension values

Sample	Absorbance
Feed (before test)	2.208
Feed (after test)	2.038
Top product (after reflux)	3.116

Table 6.2 Absorbance at 253 nm

6.2.3 Discussion

One difficulty with this experiment was the uncertainty that surfactin was definitely in the feed. Surfactin is a very powerful surfactant and with the values of surface tension measured the feed should have been around the CMC. It would therefore be expected that the feed solution would have successfully foamed with the range of air flow rates used for the CPC tests.

One possible explanation is that surfactin was not present or that other compounds within the feed were affecting its foaming properties. It was also observed by Dr Arjun Wadakar, who produced the surfactin solution, that the solution had shown more foaming the day the solution was made. This suggests that the solution had in some way changed overnight. Finally the surfactin is produced using a culture containing a variety of salts and glucose. The measured surface tension of this was 49 mN/m. The surface tension of distilled water is 72.5 mN/m. The concentration of surfactin cannot therefore be accurately estimated from the surface tension.

The experiment did show that the concentration of the feed was increased and that reflux increased the concentration of the top product. The absorbance peak at approximately 253 nm shows a definite increase in absorbance for the top product, and a decrease for the depleted feed. It is unfortunate that the exact concentrations of surfactin cannot be determined, but the experiment shows that enrichment was achieved. Also reflux enhanced the enrichment, and allowed greater separation by stabilising the foam in the riser.

7 Further Work

This project was successful in introducing controllable reflux into a column under a number of different conditions. There is however, potential to further explore the use of reflux.

For further experiments it would be useful to investigate a wider range of reflux ratios to gain insight on the relationship between the ratio and enrichment. It would also be interesting to compare specific reflux ratios for different air flow rates. Carrying out the forced drainage experiments outlined in Stevenson (2006) would allow the unknown constants for CPC to be calculated and an assessment of the column performance based upon the analysis in Stevenson *et al* (2006). The other columns that were produced could also be used to further investigate multi-stage design.

The effect of altering the height that reflux is returned to the column would worth investigating. The results indicate that as flow rates increase the effectiveness of reflux entering the column from the top reduces. Experiments with reflux entering the column at each different sample point would establish if there was any benefit in column performance by altering reflux position.

The experiments could be improved through altering some of the equipment used. If two identical or similar pumps were used for feeding the bulk solution in and taking the waste bulk away then the flow rates could be matched. This should allow true continuous conditions to be used because a slower flow rate of waste would mean the volume of solution needed would be less.

Foam breakage was a problem with this project. The motor and the build up of foam needed attention during testing, which limited the opportunity to set an experiment running and leave unattended. If true foam breakage was achieved along with true continuous conditions experiments could be run for longer allowing a better understanding of when steady state is reached. The use of ultrasound to break the foam is one possibility or the use of chemical antifoams. However, antifoams could affect biosurfactants, which would limit their use in real applications.

8 Conclusions

The aims of the project were:

- Set up and establish consistent measurements and test procedure for the new equipment
- Successfully introduce a controlled amount of reflux into the column
- Investigate the effects of reflux on the enrichment of surfactant.
- Obtain a set of experimental results for the column's concentration profile and liquid hold up.
- Measure dispersion of liquid in the column
- Use the experimental behaviour to analyse the column's performance.

The aims were in the main met, although it was not possible to calculate the number of equilibrium stages because the flow of interstitial liquid upwards could not be calculated.

The new design was a success with the problems with obtaining a top product overcome. This allowed for controlled amount of reflux to be returned to the column. Concentration and liquid hold up values were obtained for a variety of conditions and demonstrated that increasing the reflux ratio increased the enrichment. The result at the highest gas flow rate used (2 L/min) showed little improvement in enrichment when reflux was added, suggesting that at higher gas flow rates the enriching effect of reflux is not as beneficial. This is probably due to the distribution of reflux being reduced as the foam moves through the column more quickly. A direct comparison of different reflux ratios for a larger range of gas flow rates would establish how much difference different gas flow rates make on enrichment through reflux.

The time taken to reach steady state was investigated for a refluxing column and a column without reflux. The results confirmed that a refluxing column takes longer to reach steady state.

Dispersion of liquid in the column was measured with dispersion coefficients obtained. The results confirmed Swain's (2005) observation that with increasing superficial gas velocity dispersion increases. As the effect of dispersion is to reduce the concentration gradient of the column reflux may be more effective at lower gas velocities.

It was demonstrated that foam fractionation works on a biosurfactant broth and that by using reflux weak biosurfactant solutions could be separated because the reflux stabilises the foam. This confirms the potential of foam fractionation for biosurfactant separation.

9 Acknowledgements

I would like to thank everyone who helped me throughout this project, particularly Dr Martin for his support and input over the year. Also many thanks to John Hastings and the workshop for their help in producing equipment and advice. Thanks to Dr Arjunn Wadakar for providing me with surfactin broth to separate and his help throughout that experiment. Finally thanks to James Winterburn and Alasdair Walker for their company in the lab through the year.

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11 Appendices

The appendices that follow are:

Risk Assessment	Foam Fractionation				Page 1 Of of
In Building	Thom Building				
Assessment	David Wall	Signe	D. Wall	Date :	20/10/06
Assessment	Peter Martin	Signe	P. Martin	Date :	20/10/06

Hazard	Persons at Risk	Risk Controls In Place	Further Action Necessary To Control Risk
Air Supply (over pressuring equipment).	Myself.	As riser is not pressure tested, ensure the riser outlet is not blocked. There is a pressure regulator on the air supply line.	
Glass ware.	Myself and others in the lab.	Ensure that due care is taken handling glass objects, and also make sure that rotating machinery is set up correctly. In the event of broken glass, ensure that any shards are cleared away immediately. Do not work with broken glass.	
Water & electricity.	Myself and others in the lab.	Failsafe Reed breakers fitted to distribution system. Nevertheless should ensure that no electrical leads, or plugs, are placed in areas where water could accumulate.	
Climbing up to fix equipment on bench.	Myself.	Use of a kick stool	
Domestic surfactant (CPC).	Myself.	Irritant but not considered hazardous given usage.	
240 VAC Electrical shock	Myself	Equipment PAT tested by electronics	Supervisor to check validity of PAT test label and contact electronics if past label date.

Your E-mail Address: david.wall@mansfield.ox.ac.uk Checked by D J Reed date 20/10/06

Appendix B Interim Progress Report

Description of project

Foam fractionation is a separation process that makes use of the properties of surfactants to form foam. Gas is sparged through a solution containing surfactant solution. As the bubbles rise through the solution surfactant molecules absorb to the bubbles surface. These bubbles form a foam above the solution, which is channelled up a riser. This foam is then collapsed and an enriched product collected. This process has the potential to cut the cost of producing biosurfactant products such as surfactin (currently costing over £6000/g).

Previous year's work has established problems with achieving a controlled level of reflux and with the operating range of the fractionation columns leading to very dry foams. New multi-stage equipment has been designed to try and ensure that these problems can be overcome. The project will aim to measure experimentally the effects of different levels of reflux and the mixing of the down flowing liquid with the entrained liquid in the foam. These results will hopefully be valuable in establishing a model of the columns behaviour.

Results achieved so far

To gain an understanding of foam fractionation and the projects that have been run previously on the subject I have read the available project reports from over the last 6 years. I have also read literature on the subject. From this I have developed a better understanding of the theory and the experimental techniques used to investigate foam fractionation.

With Dr Martin I have helped design the new equipment and had a prototype produced in the department's rapid prototyping machine. I conducted some experiments with this, which helped establish problems with the design. This led to a few changes in the design to help resolve the problems.

Due to delays the new equipment was not ready until part way through Michaelmas term and there are still delays in smaller components to complete the experimental set-up. To reduce the amount of time getting used to the procedure for running experiments I have set up and run three of the different foam fractionation columns used for previous 4YPs. I have also familiarised myself with the experimental techniques established for last year's project. This means that when the experimental set-up is complete I should be able to quickly resolve any operating problems and begin experiments.

With the new columns I have developed fittings to ensure that it can be set up safely and operated. The new containers for the feed and top product cannot be simply clamped and have had to be fitted into cored rubber bungs to allow clamping.

I have learnt how to use the UV spectrometer to measure the concentration of CPC (the primary surfactant to be used) and have established a calibration curve for it. I have also learnt how to use the surface tension meter and have obtained a calibration for the effect of CPC concentration on surface tension.

Problems

The main potential problem is the failure of the foam breaker to break the foam, particularly at high flow rates. This has been an issue in former projects. To improve this situation the column diameter has been decreased to reduce the volume of foam the breaker has to cope with. I will also try lower concentrations of surfactant to produce a less stable foam.

The production of a large enough amount of concentrated solution from the column to carry out reflux may also cause problems. To address this I will try to run the column so that it produces wetter foams.

Future work

Week 7,8 MT: Finish production of foam sampling tubes. Set up conductivity sampling points within one of the columns. If there is time establish the feasible operating range of column.

Winter break: Finish establishing feasible operating range of column. Read over modelling the behaviour of foam fractionation columns.

Week 1,2 HT: Begin experiments to introduce a controlled amount of reflux into the column. If this is successful I will try alternate reflux ratios.

Week 3,4 HT: Continue reflux experiments. Try different concentrations of surfactants and multi-stage experiments.

Week 5,6 HT: Continue experiments.

Week 7,8 HT: If the results are consistent enough I will try to model the behaviour of the column. Begin write-up

Spring Break: Complete draft report write-up.

Week 1,2 TT: Finish final report.

Appendix C Sources of error

This appendix shows estimated sources of error and how errors were calculated.

- Mass balance +/- 0.01 g
- Spectrophotometer +/- 0.0005
- Sampling time – human error using a stopwatch. Estimated at +/- 0.2 s, when averaged over several readings estimated at +/- 0.3 s

The errors were then calculated by working out the maximum and minimum values for each measurement. Table D.1 shows an example of the maximum and minimum possible values for the masses of the test tubes used for the foam sampling and for the flow rates through them.

	Mass (g)	Time to draw down tube	Flow rate (ml/s)	Flow rate (L/min)
Test tube 1	101.64	1.60	1.03	0.062
Test tube 2	95.14	1.60	1.03	0.062

Errors					
Mass		Time to draw		Flow rate	
Min	Max	Min	Max	Min	Max
101.62	101.66	1.57	1.63	1.01	1.05
95.12	95.16	1.57	1.63	1.01	1.05

Table D.1 Calculations of error

The maximum and minimum values were calculated for all variables and used to calculate maximum and minimum concentration and liquid hold up values.

Appendix D Dispersion Coefficient Calculation

The following data shows how the conductivity responses were used to calculate the dispersion coefficients

Test 1	S(1*10&-7)					
Sample Point 2						
t	C	Adjusted C	dt	t*C*dt	C*dt	C*(T^2)*dt
1	7.89E-02	8.64E-04				
2	7.84E-02	4.31E-04	1	0.00	4.31E-04	0.00
3	7.93E-02	1.30E-03	1	0.00	1.30E-03	0.01
4	7.92E-02	1.18E-03	1	0.00	1.18E-03	0.02
5	7.92E-02	1.18E-03	1	0.01	1.18E-03	0.03
All data not included						
189	8.24E-02	4.44E-03	1	0.84	4.44E-03	158.61
190	8.17E-02	3.70E-03	1	0.70	3.70E-03	133.55
191	8.14E-02	3.37E-03	1	0.64	3.37E-03	122.83
192	8.28E-02	4.78E-03	1	0.92	4.78E-03	176.26
193	8.36E-02	5.61E-03	1	1.08	5.61E-03	209.04
194	8.25E-02	4.51E-03	1	0.87	4.51E-03	169.67
195	8.22E-02	4.24E-03	1	0.83	4.24E-03	161.11
196	8.22E-02	4.17E-03	1	0.82	4.17E-03	160.17
197	8.29E-02	4.85E-03	1	0.96	4.85E-03	188.23
198	8.27E-02	4.71E-03	1	0.93	4.71E-03	184.77
199	8.22E-02	4.17E-03	1	0.83	4.17E-03	165.11
200	8.22E-02	4.17E-03	1	0.83	4.17E-03	166.77
201	8.21E-02	4.10E-03	1	0.82	4.10E-03	165.72
202	8.22E-02	4.24E-03	1	0.86	4.24E-03	172.88
203	8.12E-02	3.23E-03	1	0.66	3.23E-03	133.30
204	8.05E-02	2.52E-03	1	0.51	2.52E-03	104.68
205	7.92E-02	1.24E-03	1	0.25	1.24E-03	52.08
206	7.92E-02	1.18E-03	1	0.24	1.18E-03	49.93
207	8.06E-02	2.58E-03	1	0.53	2.58E-03	110.56
208	8.13E-02	3.30E-03	1	0.69	3.30E-03	142.81
209	8.12E-02	3.17E-03	1	0.66	3.17E-03	138.42
210	8.10E-02	2.97E-03	1	0.62	2.97E-03	131.05
211	8.05E-02	2.52E-03	1	0.53	2.52E-03	111.98
212	8.00E-02	2.00E-03	1	0.42	2.00E-03	89.89
Totals 22578	24.00704	7.471035932		380.9956	7.470171579	30681.39671
$\bar{t}$	51.00225					
σ^2	1505.958					
σ_θ^2	0.578941					
Column Diameter	60	mm				
Area	2827.433	mm^2				

Liquid Hold Up Fraction	0.004326	
u (superficial gas velocity)	0.025503	mm/s
L (distance above bulk liquid)	90	mm
D/uL	0.171635	
Dispersion coefficient	0.3940	mm^2/s

Appendix E Calibration Data

Concentration CPC (mM)	Absorbtion			Average
0	0.005	0.003	0.001	**0.003**
0.1	0.464	0.468	0.469	**0.467**
0.2	0.908	0.911	0.907	**0.9086667**
0.3	1.311	1.312	1.31	**1.311**
0.4	1.678	1.681	1.68	**1.6796667**
0.5	1.953	1.984	2	**1.979**
0.6	2.255	2.255	2.263	**2.2576667**
0.7	2.407	2.404	2.41	**2.407**
0.8	2.485	2.485	2.487	**2.4856667**
0.9	2.556	2.558	2.557	**2.557**
1	2.575	2.577	2.578	**2.5766667**

Table 11.1 UV Spectrophometer calibration data

Concentration CPC (mM)	log Concentration CPC	Surface Tension			Average
0		70.5	70	70	**70.16667**
0.1	-4.00	55	55	55	**55**
0.2	-3.699	52.5	52	52.5	**52.33333**
0.3	-3.523	52.5	52.5	52	**52.33333**
0.4	-3.398	50	49	50	**49.66667**
0.5	-3.301	43.5	46	48	**45.83333**
0.6	-3.222	47	47	47	**47**
0.7	-3.155	45	44.5	44.5	**44.66667**
0.8	-3.097	45	45	44.5	**44.83333**
0.9	-3.046	44	44	44	**44**
1	-3.00	44	43	43	**43.33333**

Table 11.2 Surface Tension data

Pump Setting	Flow rate (ml/min)
1	0.13
2	0.268
4	0.512
7	0.894
10	1.21

Table 11.3 Pump calibration data for x1 speeds

Pump Setting	Flow rate (ml/min)
1	1.32
5	6.55
10	12.1

Table 11.4 Pump calibration for x10 speeds