COMMERCIAL BATCHWISE PRODUCTION OF POLYESTER RESINS

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SUMMARY

The work reported in this thesis was undertaken as part of the second Teaching Company Programme set up between BIP Chemicals and Aston University. The objective of the scheme was to optimise the commercial batch production of unsaturated polyester-resins.

The chemistry of polyester resins is discussed and the commercial process is described. Laboratory investigations were carried out to establish the optimum operating conditions of the production process. In particular, the operation of the existing separation equipment installed to reduce raw material losses was examined. The use of an inert gas to protect reactants was found to significantly reduce the efficiency of the separation equipment and an investigation was carried out to minimise this effect. In addition, alternative sources of inert gas were considered, but no change was recommended under prevailing commercial conditions.

A detailed study of the separation equipment already in use on the manufacturing process revealed that much of the equipment was oversize and operated inefficiently. This led to the development of a design method for a suitable partial condenser system which was then designed and installed in the commercial process. The operation of this system resulted in raw material savings, a reduced product cycle time and an increased batch yield. The associated benefits are estimated to be in excess of £158 000 per annum and the equipment had a payback time of less than six months.

Keywords

Polyester Resins
Purging Programme
Fusion Process
Partial Condenser
Packed Column

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CHAPTER 1

INTRODUCTION

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INTRODUCTION

The work reported in this thesis represents a part of the project covered by the second Teaching Company set up between BIP Chemicals and Aston University. The objective of the scheme was to investigate the batch manufacture of unsaturated polyester resins and to make recommendations which would lead to an increased profitability of the process. Two associates worked on the scheme and the final recommendations included increasing the production capacity of the plant, reducing raw materials losses, improving product consistency and introducing a new test method which substantially reduces hold up time on the process. Finally, control parameters were considered which could enable the process to be computer controlled in the future.

The manufacture of polyester resins is a profitable operation for BIP Chemicals and new resins are regularly being developed for ever more sophisticated applications. As the resin application becomes more specialised, it is even more critical that the quality of the resin does not vary. The standard production process suffered high and inconsistent raw material losses and this was a significant cause of product variability. A laboratory investigation was carried out to establish the optimum operating conditions for the process. The use of inert gas to purge the reactor was also considered. This led to the introduction of a modified purging programme which was adopted on the manufacturing process. Consequently, it was possible to consider the use of much smaller separation equipment which would operate more efficiently.

The information obtained from the laboratory experiments and from trials on the production process was utilised to develop designs for separation equipment on two reactors. These resulted in a significant reduction in the quantity of raw materials lost from these reactors. In fact, the rate of loss from the reactors was reduced to such an extent it was possible to increase the charge, and hence the yield for each batch. In addition, the improved control on a stable process resulted in reduced cycle times, and required less attention from the process operator, even though an automatic control system had not been introduced.

The installation of this equipment has resulted in cost benefits estimated to be £158 000 per annum. However, even greater benefits are possible, if the increased plant availability is used to generate base resins for high value added reprocessed resins. It is felt that cycle times could be further reduced by the introduction of an automatic control system.

CHAPTER 2

POLYESTER CHEMISTRY

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POLYESTER CHEMISTRY

2.1 Introduction

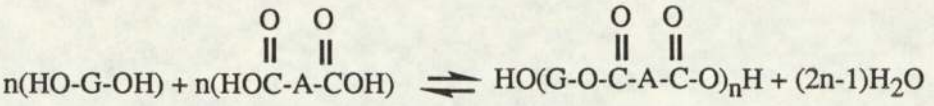
The history of polyester products begins in the late nineteenth century. In 1869, Kraut(1) first outlined the concept of a polyester chain structure. In 1894 Vorlander(2) formulated the first glycol maleates, the basis of most commercial polyesters today. However, unsaturated polyester resins were not developed for commercial applications until the late 1930's when Ellis(3) discovered that the curing rate in the final application could be increased by more than thirty times with the addition of a crosslinking monomer. A process was then developed whereby unsaturated polyester resins are used to bind together successive layers of fibre glass to give a rigid, lightweight structure. One of the first uses of these laminated products was in the production of protective covers for radar equipment during the Second World War.

After the war, polyesters were used in casting applications and later in developing dough moulding compounds where resins, fillers, fibres and catalyst are mixed together for compression moulding. These new products gave improved surface appearance and reduced the problems of shrinkage and cracking during the final cure. Since the development of these early resins, much work has been carried out to develop polyesters with special properties such as resistance to chemical attack or fire retardation, but the final method of application of the resins has changed little.

2.2 Process Chemistry

2.2.1 The Polyesterification Reaction

Polyester resins are produced by the condensation reaction between an unsaturated dicarboxylic acid and a diol. This will produce a straight chain product as shown in equation 2.1.



$$n(\mathrm{HO\text{-}G\text{-}OH}) + n(\mathrm{HO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{-}\mathrm{A}\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH}) \rightleftharpoons \mathrm{HO(G\text{-}O\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\text{-}\mathrm{A}\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{\text{-}O)}_n\mathrm{H} + (2n-1)\mathrm{H_2O} \quad .... \quad 2.1$$

The polyesterification reaction is reversible. However, the reaction takes place above 170°C and this enables the reaction to move to the right as the water of reaction is boiled off. The properties of the final resin depend on factors such as the chain length and the number of free reactive groups, among others, and so it is important that the reaction mechanism is understood. Unfortunately, because of the reaction conditions, it is almost impossible to determine accurately the kinetics of the system. This is because the reaction does not take place in an inert solvent and hence the reaction medium changes dramatically during the course of the reaction.

At the start of the reaction, the reaction medium consists of a mixture of the raw materials. This has a low viscosity and the water of reaction may be quickly removed from the reaction environment. As the reaction progresses the reaction medium becomes a mixture of raw materials and low molecular weight polyester. As the proportion of polyester increases and the chain length of the molecule grows, the reaction mixture becomes more viscous and the removal of water is hindered. Because the polyesterification reaction is reversible the presence of water in the resin body will tend to slow down the overall rate of reaction; the removal of water is, therefore, the rate determining step. Eventually, the situation will arise where the reaction medium is mainly polyester with only a small proportion of unreacted raw material. The viscosity of the reaction mixture is then normally at its greatest and the removal of the water of reaction is even further hindered.

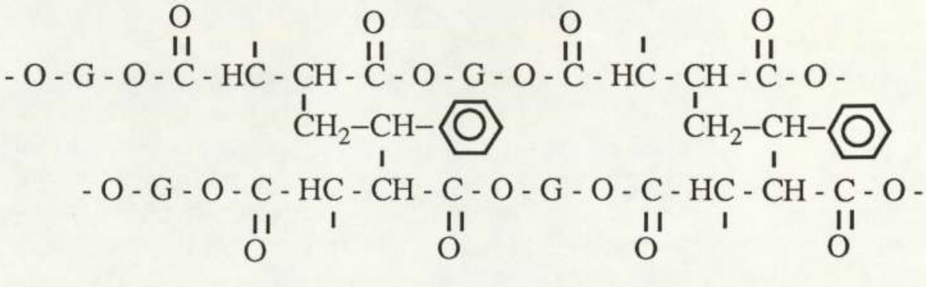
In spite of the difficulties mentioned, several workers have attempted to establish the kinetics of the reaction; however, the conclusions drawn from their work have varied significantly. Davies(4) claimed that the reaction is most closely described by second order followed by third order kinetics, whilst Flory(5) claims that third order kinetics show a better fit. Tang and Yao(6) maintain that the reaction shows two-and-a-half order kinetics. It is very difficult, therefore, to decide which of the proposed mechanisms to use as a basis for rate of reaction calculations. The rate of reaction is of particular interest to this research project because it is necessary to determine the rate of evolution of water to enable the appropriate separation equipment to be sized correctly. Because of the contradictions in the literature described above, it was decided that where required, the rate of evolution of water should be estimated from the known physical data of the raw materials and products present and from actual flowrates and stream compositions obtained in existing commercial plant.

2.2.2 The Cross-Linking Reaction

When the reaction has reached the required degree of completion, the resin is cooled to approximately 150°C. An inhibitor, such as hydroquinone, is then added to the reactor, to eliminate any free radicals which might lead to premature gellation. The resin can now be blended into the unsaturated monomer, normally styrene. Adjustments are made to ensure that the blended resin has the right balance of polymer to crosslinking monomer and, if required, stabilisers and accelerators may be added at this stage.

When the resin is required for its end use, a catalyst is added and a curing reaction takes place resulting in a crosslinked structure as shown in figure 2.1.

Figure 2.1 Structure of a Cross-Linked Polyester Resin



The curing reaction is a free radical chain polymerisation and is very exothermic. However, when laminating, the peak exotherm will be much less than this because the resin is applied in thin layers and the heat can dissipate more quickly. The gel time of the resin is defined as the time taken for the resin to set. It is extremely important that it is consistent so that the user knows how much time he has to work with the resin once the catalyst has been added. This can be controlled by the addition of accelerators and inhibitors during the blending stage of manufacture. A gel time of 15 minutes is usually sufficient for the preparation of a typical lay-up. However, when laminating it is normal to leave the product overnight between layers to enable complete curing to take place.

2.3 The Effect of Raw Materials on Resin Properties

The cured polyester structure in Figure 2.1 shows a high density of bonds linking the polyester and styrene molecules. This would result in a very brittle cured resin. If a more flexible resin is required, the spacing between the double bonds must be increased. This is normally achieved by replacing a proportion of the unsaturated acid with an equivalent molar quantity of a saturated acid. This reduces the number of cross-linking bonds and hence increases the spacing. However, it is important that the unsaturated acid is correctly distributed through the polyester molecule to ensure a complete cure. It is sometimes necessary, therefore, to modify the manufacturing process to account for the variation in acid reactivity. Occasionally, the spacing between the unsaturated bonds is further increased by selecting raw materials which have larger molecules than the basic building blocks. The following is a description of the effects of some common raw materials on the properties of the final resin. Table 2.1 gives a summary of these properties.

Table 2.1 Summary of Raw Materials Used in Polyester Manufacture

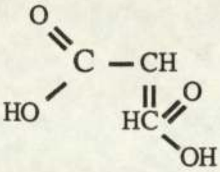
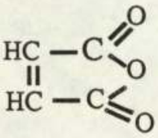
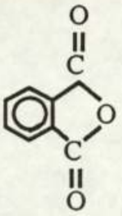
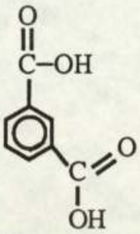
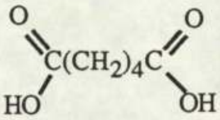
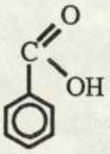
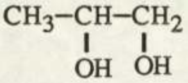
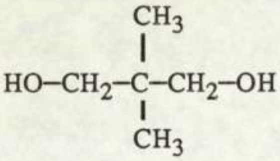
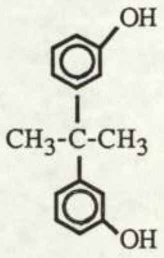
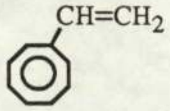
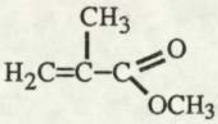
Material	Structure	Molecular Weight	Comments
1 Acids			
Fumaric Acid		116	Basic unsaturated acid building block.
Maleic Anhydride		98	Most frequently used unsaturated acid
Orthophthalic Anhydride		148	Standard saturated acid for polyester manufacture
Isophthalic Acid		166	Produces casting resins with improved temperature and water resistances
Adipic Acid		146	Used in the production of plasticising resins
Benzoic Acid		122	Chain stopping acid used to control molecular size

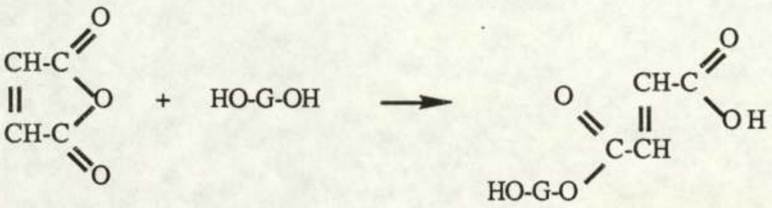
Table 2.1 Summary of Raw Materials Used in Polyester Manufacture (cont'd)

	Structure	Molecular Weight	Comments
2 Glycols			
Propylene Glycol	 $CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$	76	Standard Glycol used in polyester manufacture
Diethylene Glycol	$HO-(CH_2)_2-O-(CH_2)_2-OH$	106	Gives a resin with improved flexibility
Neopentyl Glycol	 $HO-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH$	104	Provides resin flexibility without reducing water resistance
Bisphenol A		226	Gives increased hardness and chemical resistance
3 Crosslinking Monomers			
Styrene		104	Standard cross-linking agent used in polyester manufacture
Methyl Methacrylate		100	Provides cured resin with a refractive index similar to glass

2.3.1 Unsaturated Acids

The simplest unsaturated dicarboxylic acid which can be used in polyester manufacture is fumaric acid or its isomer, maleic acid, which is normally supplied in the anhydride form.

It is known that unsaturated polyesters containing a fumaric double bond structure yield a harder resin with a higher heat distortion temperature than equivalent polyesters produced with a maleate structure. This is because the fumaric double bond is extremely reactive with the styrene monomer during the cross-linking reaction, resulting in a fast curing rate and a very strong cured structure. However, the majority of unsaturated polyesters are produced from maleic anhydride. Maleic anhydride is cheaper than fumaric acid and the use of the anhydride halves the mass of water to be removed during the process and hence reduces the reaction time. In addition, it has been discovered that most of the maleic anhydride charged isomerises to the fumaric form under reaction conditions (7, 8) as shown in equation 2.2



.... 2.2

The first stage of this reaction is the ring-opening reaction with a glycol molecule to produce the half ester. This reaction is exothermic and can produce a temperature rise of over 50°C.

2.3.2 Saturated Acids

A saturated acid is normally added to a polyester to increase the spacing between the double bonds in the polyester chains and hence increase the resin flexibility. Phthalic anhydride and isophthalic acid are most frequently used, but several others may also be used to modify the resin properties. Some of the acids frequently used are described in the following sections:

(a) Phthalic Anhydride

Phthalic anhydride is the most frequently used saturated acid in polyester manufacture. As with the maleic anhydride the reduction in the quantity of water to be removed during the reaction reduces the reaction time. The ring structure of the acid results in a compact molecule. Phthalic anhydride reacts at a similar rate to maleic anhydride and hence it is possible to charge the two acids together.

(b) Isophthalic Acid

It can be seen from the chemical structure shown in Table 2.1 that it is not possible to produce an anhydride of the acid and this leads to an increased reaction time because the exothermic ring opening reaction does not take place. It is necessary, therefore, to react the isophthalic acid before the unsaturated acid. This results in an increased reaction time since it is necessary to cool the resin between stages. The positioning of the carboxyl groups on the acid molecule improves the flexural modulus of the cross-linked polyester. Isophthalic based polyesters also produce castings with a higher heat distortion temperature, better craze resistance and improved water resistance, than those produced with phthalic anhydride.

(c) Adipic Acid

Adipic acid is a long, straight–chained saturated dicarboxylic acid. The space between the unsaturated bonds is, therefore, considerably extended and the resultant resin is extremely flexible. Adipic acid is used in the production of plasticising resins which are mixed with conventional polyesters to produce resin of greater flexibility without considerably reducing the strength of the cured resin.

(d) Benzoic Acid

Occasionally it is necessary to limit the length of the polyester molecule. This is achieved by adding a small proportion of a monocarboxylic acid such as benzoic acid. This is referred to as a "chain-stopping acid" and it ensures that the polyester molecule does not end with an active group, so preventing further reaction. This helps to control the number and size of the polyester molecules.

2.3.3 Glycols

As with the unsaturated acids, there are a number of glycols which can be used in the manufacture of unsaturated polyesters. The simplest glycol structure is that of ethylene glycol. However, ethylene glycol is rarely used in polyester manufacture because the resultant resin has a low styrene tolerance and this may result in a hazy product. For this reason it is normal to use glycols with a higher molecular weight. Some of the more commonly used glycols are:

(a) Propylene Glycol

Propylene glycol is the glycol most frequently encountered in polyester manufacture. It has the same chain length as ethylene glycol and therefore a very hard resin can be produced. The additional methyl group significantly improves the styrene tolerance. Propylene glycol has a relatively low boiling point of 187.4°C at atmospheric pressure. This is below the polyesterification reaction temperature and consequently some of the glycol is vapourised during the reaction. It is necessary, therefore, to design suitable overhead equipment which will condense the glycol vapours and return the condensate to the reactor whilst still allowing the removal of the water vapour so that the reaction can proceed.

(b) Diethylene Glycol

Diethylene Glycol is the dimer produced by the condensation of ethylene glycol. Along with similar etherified glycols it is used to increase the flexibility of the cured resin. However, the presence of an etherified glycol in a polyester also increases the water absorptiveness and consequently, etherified glycols may only be used as a part of the total charge.

(c) Neopentyl Glycol

Neopentyl glycol is also used to increase the spacing between the unsaturated bonds in the polyester chain. However, since it has no ether link in the middle of the molecule, the water absorption properties of the resin are not unduly affected and the impact resistance of the cured resin is improved.

(d) Cyclical Glycols

In some cases a proportion of the propylene glycol is replaced by a cyclical glycol such as hydrogenated Bisphenol A (2,2-di-4-2-hydroxy-phenyl propane) or cyclohexanediol. The presence of the cyclic structure results in a polyester with increased hardness. Resins with cyclical glycols are also found to have improved water and chemical resistance properties.

2.3.4 Unsaturated Comonomers

The unsaturated comonomer has a dual purpose in the manufacture of unsaturated polyesters. Firstly, it acts as a solvent for the polyester so that a mobile product may be obtained. Secondly, when the resin is required for use, the comonomer must react with the unsaturation in the polyester chain to produce a cured, thermoset product. Boenig(9) developed some general conditions for consideration when selecting a suitable comonomer. These are summarised as follows:

(a) When cured, the polyester-comonomer mixture must produce a clear, homogeneous product.

(b) The reaction between the polyester and the comonomer must be such that comonomers form cross-links between the polyester chains in preference to a homopolymerisation reaction.

(c) The comonomer must have a rate of evaporation that is low enough to be of practical interest.

(d) The comonomer must be a suitable solvent for the polyester such that the solution produced is mobile under ambient conditions.

(e) The conditions under which the copolymerisation reaction occurs must be feasible and acceptable.

(f) The peak exotherm temperature achieved during the curing reaction may be of some significance, especially in applications where a low exotherm peak temperature is necessary. However, if a comonomer meets all other criteria it may be possible to control the peak exotherm by the addition of an inhibitor.

(g) The flash point and boiling point of the comonomer must be sufficiently high to avoid safety problems.

In practice, styrene has been adopted as the comonomer most commonly used in the manufacture of unsaturated polyesters, almost to the exclusion of all others, because of its low cost and ready availability. Methyl methacrylate is occasionally used as a comonomer with styrene because it is possible to produce a resin with the same refractive index as glass which is useful for laminating panes of glass. Methyl methacrylate is rarely used as the sole comonomer because it tends to homopolymerise. It is only when styrene is present that true copolymerisation between the methyl methacrylate and the polyester takes place.

2.4 The In-Process Testing of Polyester Resins

The properties of an unsaturated resin are dependent not only on the raw materials used, but also on the reaction conditions and the degree of condensation of the resin. For example, it is possible to make two resins with very different properties from very similar initial charges. If a polyester is produced with a stoichiometric glycol charge, or a very small glycol excess, and the reaction is allowed to proceed to a low acid value, a resin with a high number average molecular weight will be obtained. By increasing the glycol charge by as little as one or two per cent it is possible to produce a resin with many more polyester molecules of lower average molecular weight. The second resin, although produced from virtually the same charge as the first, will have different properties and a different end application.

In section 2.3.3 it was explained that propylene glycol has a boiling point which is significantly below the temperature at which the polyesterification reaction takes place. It is inevitable, therefore, that some glycol losses will be experienced during the reaction, no matter what the reaction conditions or the overhead system employed.

Variations in the quantity of glycol lost during a batch may significantly affect the final resin properties. Therefore, it is necessary to monitor carefully the progress of the polyester throughout the reaction, in order that any corrective action may be taken when necessary. The polyester being produced can normally be adequately monitored by carrying out routine tests to determine the acid value and the viscosity of the reacting resin.

2.4.1 The Acid Value Test

The acid value test determines the concentration of unreacted carboxyl groups in the reaction mixture. In most cases, a sample of the polyester alkyd is made up into a solution of known concentration with styrene in the presence of hydroquinone to prevent gellation of the resin. The solution is then titrated with an ethanolic solution of potassium hydroxide. Occasionally, the titration may be carried out directly on the unblended resin, provided that the viscosity is sufficiently low to ensure intimate mixing during the titration. The acid value is expressed in terms of mg KOH/g solid resin. This is a standard test which is recognised throughout the paint and plastics industry.

2.4.2 PRS (Paint Research Station) Solution Viscosity

The viscosity of the resin can be used to follow the build-up of the polyester molecules. A low viscosity resin is indicative of a large number of small molecules, whereas a high viscosity suggests that the smaller molecules are combining to produce fewer molecules of high molecular weight. The viscosity is normally tested by preparing a solution of the resin in styrene to a known concentration. A fixed volume of the solution is poured into a straight-sided test tube known as a PRS tube and the tube is sealed. It is then placed in a water bath until it reaches a constant temperature of 25°C. When cool the tube is inverted and the time taken for the air bubble to reach the top of the tube is compared to that of several standard oils of a known viscosity at 25°C. This is also a test recognised within the industry.

2.4.3 Melt Viscosity

For some polyesters, the molecular size distribution is particularly important if the desired end properties are to be achieved. In these cases, it may be necessary to determine the melt viscosity of the resin in process. This is achieved by taking a small sample of the alkyd and testing the viscosity at a specified temperature using a cone and plate viscometer. The melt viscosity is of interest because it is sensitive to the build up of high molecular size molecules in highly condensed resins.

In all other cases, the PRS viscosity is a preferred control parameter because there is a straight line relationship between the reciprocal PRS viscosity and the acid value of the resin. This relationship can be plotted as the reaction proceeds and by extrapolation to the y-axis it is possible to predict the gel point acid value. As the acid value drops and the product becomes more highly condensed, a point is reached when further condensation is impossible and the resin can be considered as a single molecule (a gel). The resin viscosity is, therefore, infinite. This is obviously undesirable in the commercial process and hence it is necessary to match the resin formulation and the process control limits to ensure that gellation of the resins does not occur during processing.

2.5 The Commercial Manufacturing Process

The polyesterification reaction is a reversible condensation reaction. Therefore, the rate of reaction is controlled largely by the rate of removal of the water of reaction. The reaction temperature is normally of the order of 200°C and so the water evaporates from the reaction mixture. Unfortunately, propylene glycol has a boiling point of 187.4°C and will also be vapourised during the reaction. It is necessary to operate the process in such a way that the propylene glycol vapour is condensed and returned to the reactor while the water is removed from the reaction system for disposal.

As indicated in section 2.3.2, most unsaturated polyesters contain either orthophthalic anhydride or isophthalic acid. These two acids behave very differently in the reactor environment and it is not surprising, therefore, that different processing techniques have been developed for the two types of resin. The differences in the processing of the two resin types are discussed later. The following is a summary of the basic process which is similar for both resin types.

2.5.1 General Process Description

(a) Raw Material Charging

Preliminary checks are carried out on the reactor to ensure that it is clean, empty and ready for use. An inert gas purge is applied to remove oxygen from the reactor and the glycol or mixture of glycols to be used is then charged. It is important that oxygen is excluded during the polyesterification reaction to avoid unwanted side reactions. The agitator is then turned on and the glycol mixture is heated to approximately 60°C before the organic acids are charged. This is to aid the dissolution of the acids into the glycol as they are only slightly soluble at ambient temperature. The unsaturated acids are charged as solids and it is necessary to control the rate of addition to ensure that the agitator is not damaged by solid lumps. Once this operation is complete, the maleic anhydride is charged in molten form via a weigh tank. The nitrogen sparge is then switched off and a reduced flow purge is applied to the reactor dome to prevent the ingress of air. The heat can now be applied to the reactor.

(b) Reacting

The first reaction to take place between the maleic anhydride and the glycol is the opening of the anhydride ring. This reaction is exothermic and takes place at about 90°C. It is essential, therefore, that heat is applied to the reactor slowly until this reaction has been completed. Once this reaction is complete the heating rate can be increased but it must still be carefully controlled in order to minimise glycol losses. The reactor is heated to a maximum temperature of 200°C to 220°C over a period of five to seven hours. Process testing begins one hour after the top reactor temperature has been achieved but may be earlier for more sensitive resins.

(c) Process Testing

A description of the process tests carried out during the manufacture of a polyester resin has been given in Section 2.4. These tests are carried out on an hourly basis until the resin is within the processing specifications. If the acid value-viscosity relationship begins to drift from the expected results plot at any time, it may be possible to charge additional glycol or acid to the reactor in order to readjust the balance of the resin. However, this is not possible in all cases, and cannot be attempted when the resin is very close to the final processing specification, since the raw material added would not have time to react into the resin and would merely act as a diluent, taking no part in the curing reaction.

(d) Blending

When the resin has reached the required processing specification, it is cooled in preparation for blending with the unsaturated monomer, normally styrene. When the resin reaches 150°C, inhibitor is added to the resin and styrene is charged to the blender. When the resin reaches 130°C, blending can commence. Cooling is applied to the blender and the resin is charged at such a rate that the blender temperature does not exceed 60°C. This is to avoid premature gellation of the resin or monomer in the blender.

When the entire batch of resin has been charged to the blender, samples are taken to determine that the resin has the correct properties. It is likely that some adjustment to the concentration of the blended resin will be required, since the resins are initially under-diluted to allow for batch to batch variation in raw material charging and hence resin yields. Finally, it may be necessary to make adjustments to the resin gel time by the addition of inhibitor or accelerator, if appropriate.

2.5.2 The Solvent Process

Most general purpose resins are produced from a mixture of maleic and orthophthalic anhydrides. These acids are of similar reactivity and hence the resins can be produced by a single stage process. Because of the fast reactions involved, it is essential that a very efficient method of separating the water and glycol vapours is employed. For this reason a processing technique has been developed whereby use is made of an azeotropic agent to aid the removal of the water of reaction.

It is known that xylol (a commercially available solvent containing the three isomers of xylene) and water form an azeotrope which has a minimum boiling point of 94°C Above the reactor there is a fractionating column through which all vapour generated in the reactor must pass. Therefore, by maintaining the column top temperature at 94°C, by adjusting the reflux and heating rate, it is possible to remove the water of reaction without undue losses of propylene glycol. The azeotropic mixture is then condensed and fed to a separator. When cold, the water and xylol separate into two layers and the xylol overflows into a balance tank. From here it is either returned to the top of the fractionating column as a reflux to wet the packing and enable efficient mass transfer to take place, or it is returned to the solvent tank.

When the reaction is close to completion the solvent feed and reflux are stopped and any remaining xylol in the reactor is boiled out of the resin mixture and returned to the solvent stock tank. It is important that all xylol is removed from the resin before the resin is blended with styrene. This is because residual xylol in the blended resin adversely affects final curing.

Although the reduction in the boiling point is minimal compared with the difference in the boiling points of propylene glycol and water, the solvent process is preferable to a conventional distillation process, where it is normal practice to reflux condensed overhead vapours. This is because it is possible to feed an organic reflux to the top of the column rather than an aqueous mixture. This is particularly important since the use of an aqueous reflux results in an increased quantity of water being returned to the reactor and consequently the reaction time is increased.

2.5.3 The Fusion Process

In some cases it is not possible to use an azeotropic agent to aid the removal of water. This may be because of the raw materials used, or because the end application of the resin will not tolerate even the smallest concentration of xylol in the final product. This is particularly important if the final moulding is to be used in the food and beverages industry.

The process which does not use an azeotropic agent to remove the glycol from the vapours leaving the reactor is known as the fusion process. The fusion process has become much more significant in recent years as the range of resins developed for specialist applications has been extended. This has meant that the resin properties must be more consistent and in many cases the resin must have the correct proportions of different molecular weight fractions as determined by gel permeation chromatography. To produce a resin to a very precise specification it is necessary to be able to control the reaction conditions and the rate of loss of glycol very carefully.

Without the use of an azeotropic agent to aid the separation of glycol and water vapours, it is necessary to rely on suitably designed separation equipment and the correct operating conditions to ensure a repeatable product. This may be achieved by the use of partial condenser systems. This type of system consists of a shell and tube heat exchanger below which there may be a packed section. Typically, the vapour from the reactor passes through the packed section and into the tube-side of the heat exchanger. Either steam or water can be used as the coolant in the shell of the exchanger. A temperature indicator is sited in the vapour duct at the top of the heat exchanger and the temperature of the vapour leaving the system is controlled by adjusting the rate of flow of coolant. If heat and mass equilibrium are reached within the system, control of the temperature of the exit vapour should also control the vapour composition. In this way it should be possible to account for the losses of glycol from the system.

It is this type of overhead system which is of particular interest in this research project. It is planned to improve the performance and flexibility of the polyester plant by introducing a purpose-designed separation system onto an existing reactor. It is the purpose of this research project to determine which system would be the most effective to install, and consequently to propose a design procedure to identify the optimum operating conditions.

CHAPTER 3

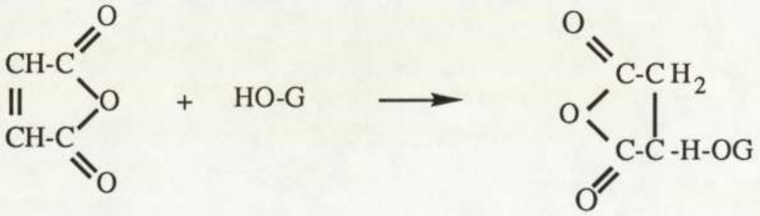
THE IMPORTANCE OF AN INERT ATMOSPHERE DURING THE MANUFACTURE OF UNSATURATED POLYESTER RESINS

CHAPTER 3

THE IMPORTANCE OF AN INERT ATMOSPHERE DURING THE MANUFACTURE OF UNSATURATED POLYESTER RESINS

3.1 Introduction

As mentioned in Section 2.5, it is essential that the manufacture of unsaturated polyesters takes place in an inert atmosphere. It is known that the presence of oxygen during the reaction stage promotes the addition of glycol molecules across the unsaturated bonds in the maleic anhydride as shown in equation 3.1:



...... 3.1

It is estimated by Felici(10) that this reaction destroys approximately ten per cent of all unsaturated bonds during a normal polyesterification reaction when carried out in an inert atmosphere. The presence of oxygen may cause further reaction resulting in up to thirty per cent of unsaturated bonds being destroyed. This has a detrimental effect on the final resin, as the increased branching of the polyester molecules results in an increased resin viscosity. In addition, the unavailability of unsaturated bonds adversely affects the properties of the cured resin, since the reduction in the number of reactive sites results in a weakened structure. Finally, the presence of oxygen, particularly in the late stages of the reaction, may cause discolouration of the resin which would result in the resin being undesirable for certain applications.

Initially, polyesterification reactions were carried out under a continuous high flowrate of very high purity inert gas in order to avoid the unfavourable chemical reactions described. Early reports(11) describe a flowrate of 1132 dm^3/min of inert gas containing not more than 0.02 % oxygen by volume for an 8.5 tonne batch of polyester resin. However, the non-condensable gas acts as a carrier for volatile vapours and high gas flowrates at elevated temperatures result in the loss of volatile raw materials from the reaction mixture. Such high flowrates were possible when both inert gas and raw materials were cheap and environmental awareness was not so acute. In addition, the molecular weight distribution of the early unsaturated resins was not so critical as it is now and glycol losses could easily be made up during processing without significantly affecting the product quality. Consequently, very little effort was made to minimise the loss of raw materials from the reactor and exhaust vapours were simply vented to atmosphere.

In the manufacture of modern unsaturated polyester resins, it is no longer acceptable to lose glycol from the reactor as this has a significant affect on both the quality and the economics of the resin. Therefore, equipment is used which is intended to condense the glycol vapours and return them to the reactor without inhibiting the rate of removal of the water of reaction. However, the presence of a non-condensable gas in a vapour flow is known to affect seriously the efficient performance of mass and heat transfer equipment(12). This is particularly important in condensation equipment. In a well designed condenser the rate determining step is the heat transfer between the vapour film and the tube wall or liquid film with which it is in contact. Turbulent flow of the vapour stream will ensure rapid replacement of the vapour film. Once a non-condensable gas is introduced into this system, the rate determining step becomes the diffusion of the vapour through the gas to reach the tube wall or liquid film before condensation can take place. This diffusion step may be slower by up to a factor of ten, making it necessary to design equipment with a much larger heat transfer area, increasing the capital cost of the plant

Finally, an investigation into the annual cost of purging the polyester reactors indicated that any reductions in inert gas which could be made would result in significant savings. Therefore, a review of the alternative sources of inert gas was undertaken and an investigation was carried out into the efficiency of the purging programme and its effects on raw material losses. A further investigation was then carried out into the effects of the composition of the inert gas on the quality of polyester resins.

3.2 Inert Gas Systems

There are several factors which must be taken into account when considering the source of inert gas to be used in polyester manufacture. Firstly, it is essential that the oxygen content of the gas is sufficiently low and that the quality of the gas is consistent. Secondly, because of the impact of oxygen on the resin quality, it is likely that resin production would have to cease in the event of an interruption in the supply of inert gas to the polyester reactors. It is necessary to ensure, therefore, that any supply system of inert gas has full back-up facilities to ensure continuity of supply. A third factor for consideration is safety. Inert gases are asphyxiants by definition and it is necessary to ensure that adequate ventilation is available around the gas generator or storage vessel and at the vents from the reactors. In some cases the inert gas may also be flammable in which case it is necessary to collect all vent gases and ensure their safe disposal. Finally, it is necessary to consider the economics of the process. The most cost effective method of inert gas generation should be employed provided that the other criteria for selection can be adequately met. In addition, the consumption of the gas should be monitored to ensure that it is being used efficiently. The following is a description of some commercially available sources of inert gas.

3.2.1 Cryogenic Nitrogen

Cryogenic nitrogen is produced by the liquefaction of air. The difference between the boiling points of oxygen and nitrogen makes it possible to produce a gas with a very low oxygen content of not more than 10 ppm. The liquid nitrogen is delivered by road tanker and stored in a vacuum insulated vessel which is usually provided and maintained by the nitrogen suppliers. When required for use, the liquid is passed through a long coiled pipe and a series of pressure reducers to enable it to vaporize slowly and reach ambient temperature. It is normal to have an agreement with the liquid nitrogen suppliers whereby they undertake to provide a round-the-clock emergency supply of nitrogen and maintenance service.

The very high quality of the inert gas supplied and the guarantee of an emergency service means that the cryogenic nitrogen system is very reliable. However, the tank and the evaporator lines may require a lot of space which must be completely fenced off to avoid the possibility of rupture of the tank as a result of impact by moving vehicles. Cryogenic nitrogen is also very expensive because of the high cost of the cryogenic process and because of the quality of the service assured.

3.2.2 Solid Carbon Dioxide

It is possible to use solid carbon dioxide in a way similar to that described in the previous section for liquid nitrogen. In this case, solid blocks of carbon dioxide, commercially known as "Dri-Kold", are evaporated to provide a high quality inert gas. This method is not as desirable as the cryogenic nitrogen because more direct contact with the very low temperature material is required and hence safety is of some concern.

3.2.3 Stoichiometric Burners

It is possible to generate an inert gas supply on site by the use of a stoichiometric burner, which works by burning oil or natural gas in a limited volume of air. The air rate is controlled so that sufficient oxygen is available to combust the fuel completely without an excess in the exit gas. The product gas consists mainly of nitrogen and carbon dioxide with traces of carbon monoxide and argon, together with fifteen to twenty per cent water vapour at this stage. Moisture would be unacceptable in an inert gas supply for use in unsaturated polyester manufacture and this could be removed by passing the product gas through a chiller; hence condensing out the water vapour.

Stoichiometric burners are a very efficient way of producing inert gas, particularly when large supplies are required, thus making heat recovery a viable option. It would, however, be necessary to consider emergency sources of supply in the event of a burner failure or during maintenance.

3.2.4 Pressure Swing Adsorbers

An alternative method of generating inert gas locally is the production of nitrogen by the operation of a Pressure Swing Adsorber (PSA). A PSA unit consists of two beds of carbon molecular sieves which preferentially adsorb oxygen from compressed air. The carbon molecular sieves are only capable of adsorbing a limited volume of oxygen before they must be regenerated, so two chambers are used. In this way it is possible to desorb the oxygen from one bed while the other is adsorbing, thus providing a continuous product flow. As the name implies, adsorption takes place under pressure and to improve the cycle time of the unit, a portion of the product gas from one adsorber is fed into the second adsorber at the end of each cycle to equalize the pressure between the two beds.

A major advantage PSA units have over other methods of inert gas generation is that the unit can be designed to produce gas of whatever quality is required. This is possible because the oxygen content of the inert gas is a function of the flowrate of air through the unit. Nitrogen can be produced up to a purity of 98.5%; the balance of the gas consists mainly of argon and it is possible to produce an inert gas of less than 0.1% oxygen by volume, however, a value of 2% is quite typical. The flexibility of the PSA system may also be a disadvantage since fluctuations in operating conditions may result in a variation in the quality of the product gas. It is necessary, therefore, to analyse the quality of the product gas and to sound an alarm if the oxygen should rise above predetermined limits.

Finally, the carbon molecular sieves contained within the PSA units are extremely sensitive to the presence of oil and moisture. It is important, therefore, that the feed gas to the unit should be clean and dry and that necessary filters should be installed to protect the unit.

3.3 Established Purging Programmes

Prior to the start of this research project, two different purging programmes were in use commercially to exclude oxygen from the polyester reactor environment. In both cases, cryogenic nitrogen was used as the inert gas. In addition, a lower quality inert gas was used to reduce the oxygen content in the blenders while the resin was being blended in styrene and adjusted into specification. This secondary inert gas supply is provided by a Pressure Swing Adsorber designed to provide a product gas containing two per cent oxygen.

3.3.1 The Fusion Process

The purging programme adopted for use during the fusion process consisted of a small continuous flow of nitrogen into the reactor. During the charging of the reactor this flow would be directed to the bottom of the reaction vessel as a sparge, in order to remove any air which may have been entrained in the raw materials during the transfer process. Once charging had been completed, the nitrogen sparge was stopped but the same flowrate of inert gas was applied to the dome of the reaction vessel to prevent the ingress of air through the overhead equipment. The reaction was then progressed as described in Section 2.7. Most polyester reactions slow down significantly towards the end of the process as the remaining water of reaction becomes more difficult to remove. When this happened, the nitrogen flow was directed back to the base of the reactor and the flowrate increased by up to six times. The vapour leaving the reaction mixture was then removed from the reactor system via a by-pass condenser if fitted. The high flowrate sparge through the reactor contents would drive off any remaining water of reaction and hence speed up the reaction. Any unreacted glycol would also be stripped from the reactor by this process and so it is important that this stage is not commenced too early in the reaction.

3.3.2 The Solvent Process

The purging programme actually operated during the charging and heating up stages of the polyesterification reaction was very similar to that previously described for the fusion process. However, in this case the flowrates used were three to four times higher than those used in the fusion process. Once the solvent feed to the reactor had commenced and distillation had begun, the inert gas purge was stopped altogether, since the vapour space in the reactor system was full of xylol vapour which is also an acceptable inert material for this application. The nitrogen flow was reapplied as a sparge towards the end of the reaction to assist in the removal of xylol from the reaction mixture. It is thought that the high initial purge rates were originally adopted to be quite sure that all traces of oxygen were removed from the reactor environment before the nitrogen purge was stopped.

3.4 Optimisation of the The Purging Programme

3.4.1 Introduction

A review of the use of inert gas on the polyester plant highlighted several inconsistencies and it was felt that improvements could be made. The ideal purging programme would be suitable for all manufacturing processes and would use the minimum volume of inert gas. It was felt that a consistent purging programme would result in a more consistent performance of the reactor overhead equipment and consequently a more consistent rate of loss of raw materials. This would have a direct affect on the quality of the polyester produced. However, the reactor atmosphere must remain sufficiently inert to avoid the unwanted side reactions previously described.

It was decided to carry out a laboratory investigation into the effect of the inert gas purge on the quality of the final resin and on the efficiency of the glycol-water separation equipment. The results of this work could then be taken into account when considering the design for new overhead separation equipment and it may be possible to specify equipment significantly smaller than that currently employed. A series of experiments was carried out in the laboratory into the effects of various purging programmes on the first stage of a two stage fusion process resin, hereafter referred to as resin A. The first stage of the resin was selected for consideration because process experience showed that most glycol losses occurred early on in the reaction. This is thought to be due to the very high concentration of unreacted glycol present in the reaction mixture at the beginning of the process.

3.4.2 Equipment

The purging programme experiments were all carried out in two litre, round-bottomed glass reactors. Heat was provided by an electric isomantle. A temperature controller with a thermocouple and a digital display was used to control the temperature of the reactor contents. The reactor and lid were sealed with a commercial sealing agent to prevent the ingress of air or the leakage of propylene glycol vapour. In order to determine directly the effect of the inert gas purge on the loss of glycol from the resin body, no separation equipment was used in the first instance. Instead, a total vapour condenser was installed to enable the detection of any variations with reaction time of the composition of the vapour leaving the resin mixture. Agitation was provided by a variable speed anchor stirrer. Inert gas was fed into the reactor through a glass tube, which was angled slightly into the direction of rotation of the agitator to help prevent blockage by undissolved acid crystals. For the final run in this experiment the equipment was modified slightly. In this case a continuous purge was not being applied to the reactor and therefore it was necessary to provide a water seal in the vapour line to prevent the excessive ingress of air. Schematic diagrams of the reactor layouts are shown in figures 3.1 and 3.2

3.4.3 Inert Gas Flowrate

The inert gas used in this investigation was bottled "white spot" nitrogen which has an oxygen content of not more than 8 vpm. The rate of flow of nitrogen into the reactor was measured by differential pressure, using a traditional piece of equipment having a reservoir of glycerol into which a capillary tube was inserted. The nitrogen flow is then passed across the top of the capillary tube, causing differential pressure which can be detected by the difference in the glycerol levels. A scale is situated behind the capillary tube so that the differential liquid height can be recorded. From here the nitrogen is passed into a second smaller vessel also containing glycerol where the gas bubbles flow through the glycerol via a dip pipe. This gives a visual indication of flow to ensure that the

Figure 3.1 Laboratory Apparatus for Nitrogen Flowrate Experiments

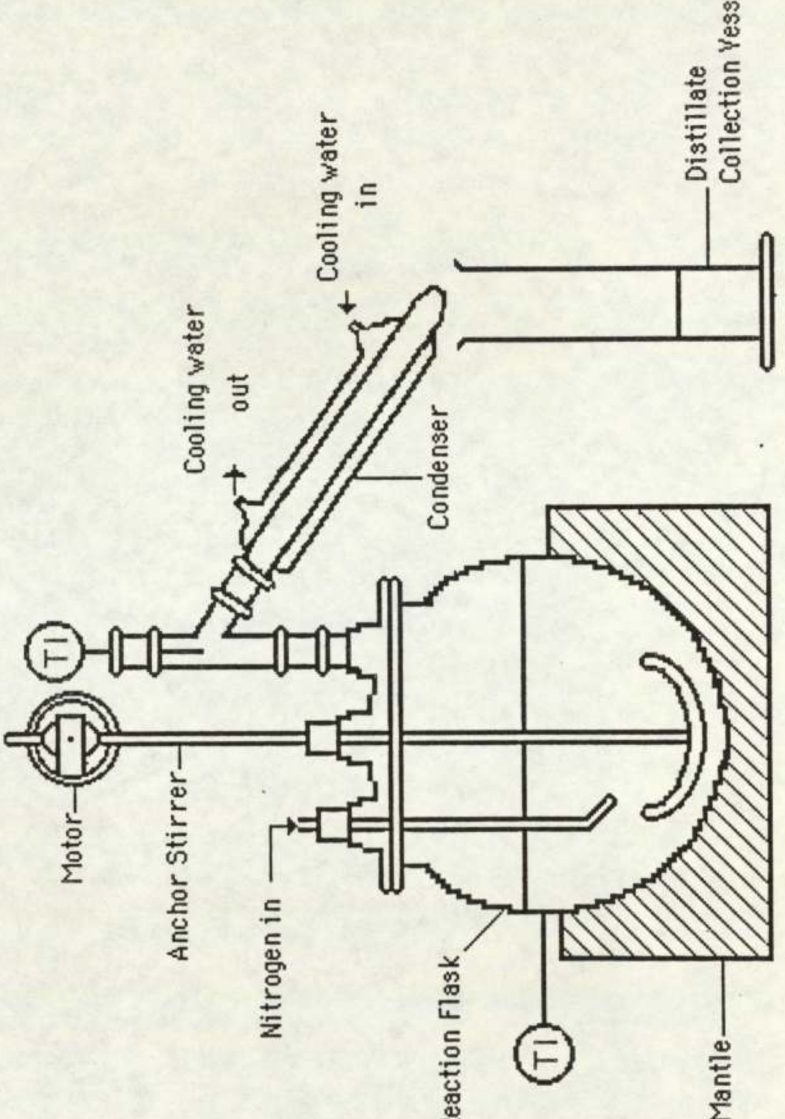


Figure 3.2 Laboratory Apparatus for Polyester Manufacture without an Inert Gas Purge

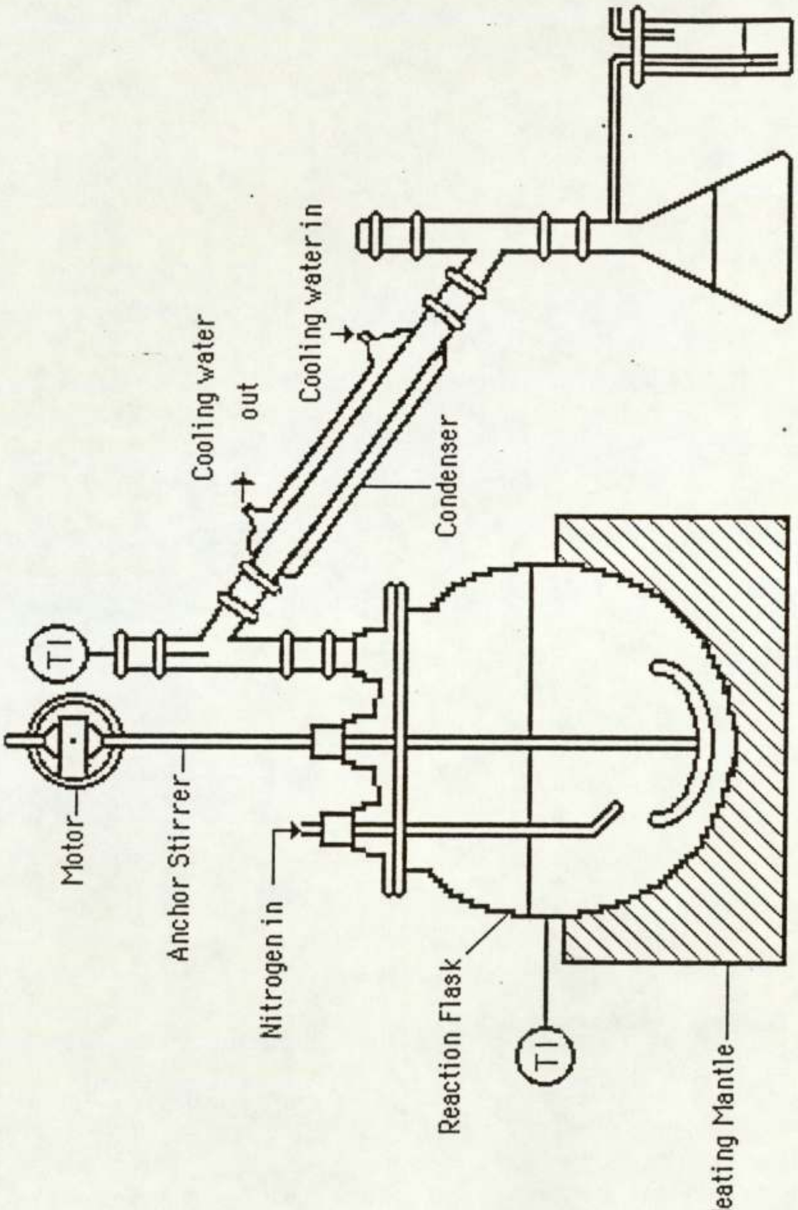
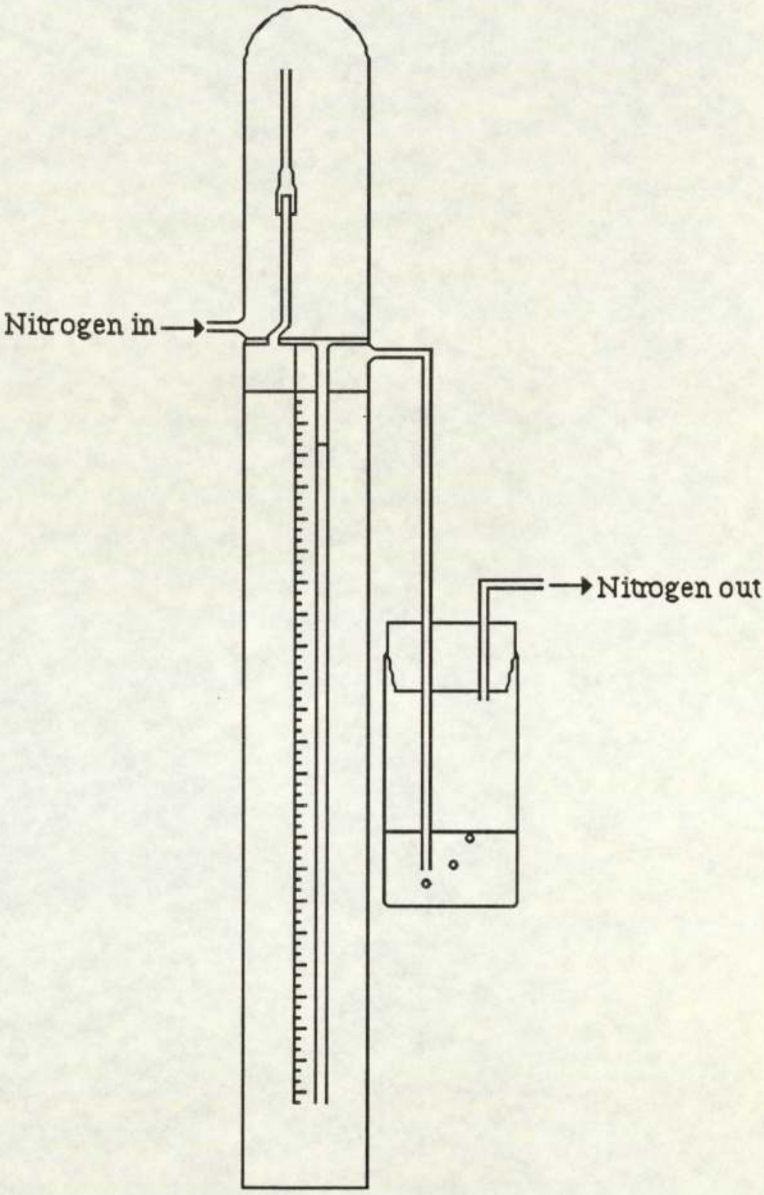


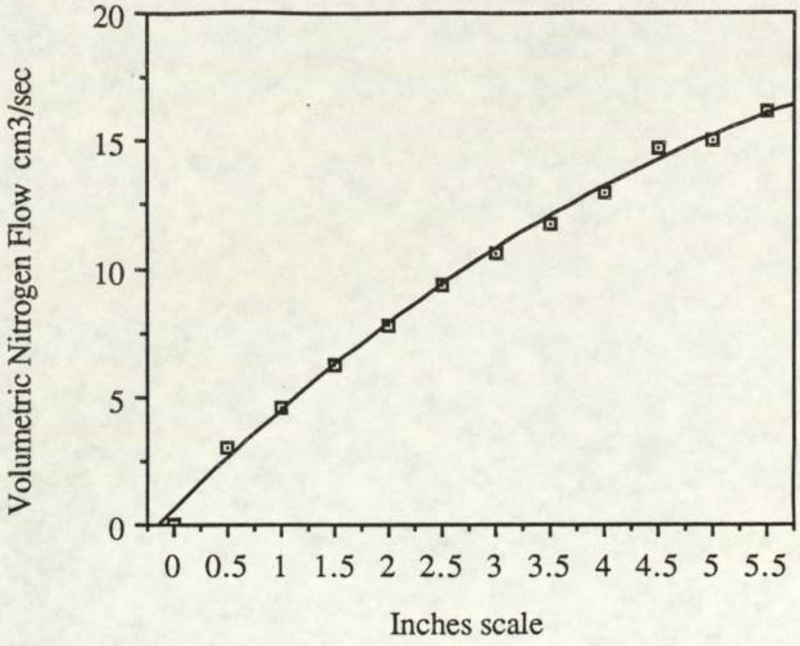
Figure 3.3 Schematic Diagram of the Inert Gas Gauge



discharge tube is not blocked. A schematic diagram of the inert gas gauge is shown in figure 3.3.

The nitrogen flow gauge selected for use in these experiments was calibrated by timing the passage of a soap bubble through a burette at various differential pressures. The calibration graph is shown in figure 3.4.

Figure 3.4 Nitrogen Flowrate Calibration Curve



3.4.4 Experimental Method

The experimental work consisted of the production of four batches of resin A under different purging programmes. In each case the process was based on the standard laboratory method for the production of resin A except that no attempt was made to minimise the loss of propylene glycol vapour from the reactor. The same batch size and formulation was used for each run. In addition, the rate of heat input was kept as constant as possible although some fluctuations were unavoidable especially at high nitrogen flowrate.

The first three runs were produced under a constant nitrogen purge. During each of these runs the rate of removal of distillate and the composition of the cumulative distillate collected were recorded. The flowrates used for these batches were 3 cm^3/s, 13 cm^3/s and 1.6 cm^3/s respectively. 3 cm^3/s corresponds to the standard inert gas flowrate used in the laboratory. 13 cm^3/s is the gas flowrate normally sparged through the resin at the end of a laboratory scale batch to aid the removal of water. 1.6 cm^3/s was selected as the third flowrate for investigation because it is the lowest flowrate which can be measured on the available equipment in the laboratory. However, it also approximates to the equivalent flowrate used on the manufacturing scale based on the weight of raw materials charged.

In all cases the purge was initially applied to the vapour space in the reactor. However, towards the end of the reaction a gas sparge assists in the removal of water from the reaction mixture. Therefore the gas was passed through the resin during the later stages of the reaction when necessary. In some cases it was also necessary to increase the sparge flowrate at the end of the process in order to take the reaction to completion. The normal processing conditions for the production of polyester resin in the laboratory use a continuous nitrogen flowrate of 3 cm^3/s and this was adopted as a minimum flowrate for use when the reaction vessel was open to the atmosphere during sampling.

For the fourth batch, the equipment was modified slightly to reduce the ingress of air into the system. In this case a continuous purge was not applied. Instead, the reactor was purged before charging and during the initial heat up. The nitrogen purge was then applied only when the resin was exposed to the atmosphere during testing and on cooling although a sparge was applied as usual towards the end of the process. It was not possible to measure the rate of removal of the distillate or determine the distillate composition during the processing of this batch because of the necessity of keeping the vapour line sealed. Therefore, only total values are available.

Finally, because of the long reaction time it was necessary to carry out each of these trials over several days. At the end of each day it was necessary to cool the resin. In order to prevent the ingress of air and the subsequent discolouration of the resin, a nitrogen purge was applied to all resins on cooling and a very low purge rate was applied through the night.

3.4.5 Analysis of the Distillate

Some difficulty was encountered in finding a quick and accurate method for determining the composition of the distillate which was suitable for use during the experimental batches. Therefore, the distillate was assumed to be a two component mixture and the glycol composition was calculated from its density and the refractive index. The calibration curves for both methods are shown in figures 3.5 and 3.6 respectively. Whenever the two methods gave different distillate compositions an average result was used. In general the two methods gave agreement within two mass percent although much larger deviations could be obtained at the end of the process and at very high inert gas flowrates.

3.4.6 Results

Table 3.1 gives a summary of the results obtained during these experiments. It can be seen that in each case the reaction time and the acid value at the end of the first stage have been given. Because the rate of reaction depends very much on the processing conditions and the resin will continue to react slowly during cooling, it is very difficult to stop the reaction at the same point on each run. Therefore the calculation of the loss of glycol for batch 2 has been based on an acid value of 10.5 mg KOH/g rather than the final attained acid value of 4.3 mg KOH/g. The final value has been included so that the reaction times can be compared.

Figure 3.5 Aqueous Propylene Glycol Solution (Composition *vs* Density @ 25°C)

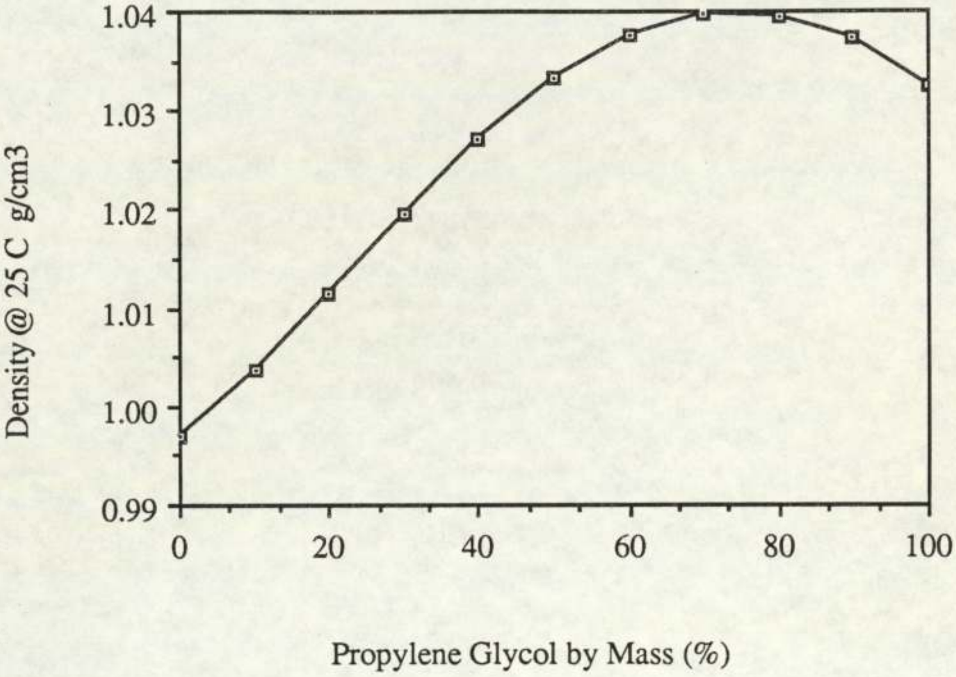


Figure 3.6 Aqueous Propylene Glycol Solution (Composition *vs* Refractive Index @ 25°C)

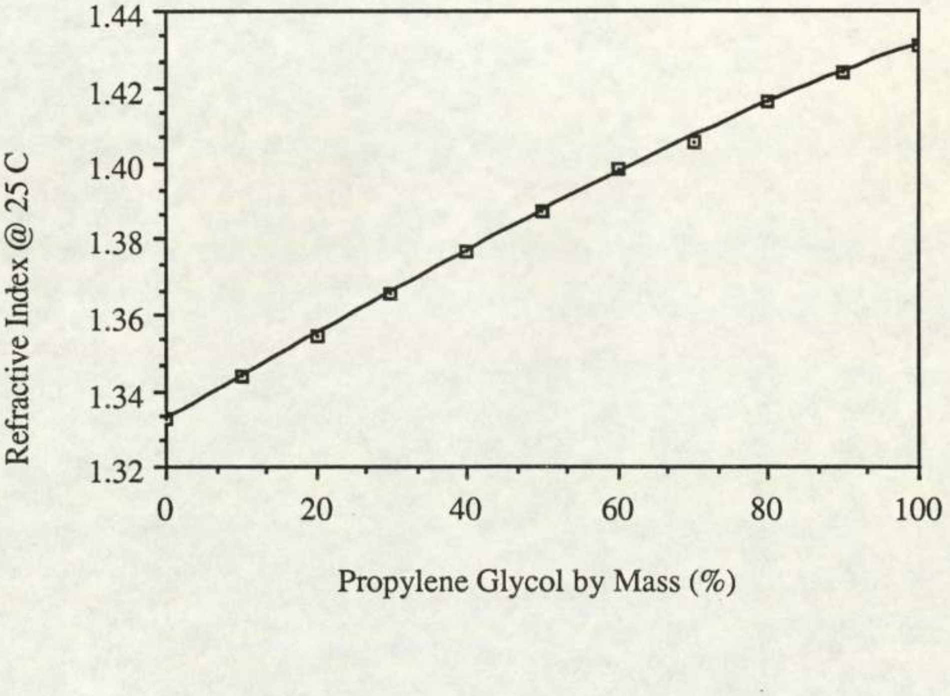


Table 3.1 Summary of Results from Nitrogen Flowrate Experiments

Batch no	N_2 Flowrate (cm^3/s)	Reaction time (hrs)	Acid value (mgKOH/g)	Glycol loss at end of stage 1	
				weight (g)	% of charge
1	3	7.5	11.9		
		9	5.3	16.68	3.1
2	13	10.5	8.16		
		12	4.3	90.14	16.9
3	1.6*	7.5	7.47	7.73	1.4
4	0*	10.5	6.12	29.3	5.5

* Nitrogen flowrate was increased to 3 cm^3/s when the reactor contents were exposed to the air.

3.4.7 Discussion

The results for the first three runs given in Table 3.1 show that the first stage of the reaction progresses more quickly and less propylene glycol is lost from the reaction mixture when a lower nitrogen flowrate is used. It was found that the increased nitrogen flowrate used in run number 2 made the process very difficult to control. Very small changes in the rate of heat supplied to the reactor had very significant effects on the vapour temperature and frequently resulted in the condenser being overloaded. Consequently it was often necessary to reduce the heat input to the reactor in order to avoid the uncontrolled loss of glycol .

Run 3 was operated with a very low nitrogen flowrate. The operating conditions for this batch were found to be much more stable and easier to control than for those batches using higher flowrates and this is thought to have contributed to the increased reaction rate.

For experimental batches 1 and 3 the second stage of the reaction was also carried out so that the effect of the purging programme on the final properties of the resin could be considered. It is standard practice to produce all batches of polyester resin in the laboratory by the fusion process irrespective of the method of production used on the plant. In the case of resin A the second stage of the process is normally carried out by the solvent process. However, it was felt that the fusion process would be more sensitive to any changes in the purging programme and that this process would be more appropriate for these trials.

It was attempted to process the second stage of the first batch at a constant nitrogen flowrate without sparging the nitrogen through the body of the resin in the final stages of the reaction. This was unsuccessful because the distillation quickly stopped and the slow reaction rate resulted in the viscosity increasing with little change in acid value. For run 3, the nitrogen was sparged and then the nitrogen flowrate was increased as the vapour temperature dropped and the distillation rate fell. This resin was also found to be out of specification. It is suspected that the method of returning glycol to the reactor at intervals may be the cause of the failed batches since the same formulation is much more successful when used on standard equipment even when the fusion process is used throughout. The second stage reaction of batch 2 was not attempted because the high rate of loss of propylene glycol from the reaction mixture, the unstable reaction conditions and the increased reaction time for stage 1 had already made the process unviable.

The final experimental run shows that it is possible to produce a polyester without using a continuous inert gas purge. However, the equipment used for this batch included a water seal which prevented air from entering the system through the condenser. This was considered to be an acceptable modification to the equipment because of the relatively short path from the reactor to the receiver on the laboratory rig. On a production scale the path for diffusion into the reactor would be much more tortuous since the vent is located at the bottom of the total condenser. A constant purge is also less likely to be necessary on the plant than in the laboratory because of the method of sampling the resin. On the production scale it is not necessary to expose the system to the atmosphere when removing samples since these are collected from the bottom of the reactor unlike the laboratory equipment where it was necessary to sample through the lid of the reactor. Whichever scale of equipment is used, air will be drawn into the reactor during the charging of raw materials and on cooling and it is clearly necessary to apply an inert gas purge when these operations are being carried out.

The problems associated with the fourth run meant that the results do not follow the general trend described above. Because it was necessary to remove the stopper from the reactor every time a charge was made or a sample was taken, it was necessary to purge the system during this period. This sudden application of a purge was seen to have a dramatic effect on the vapour temperature which increased by over 30°C in some cases even though the inert gas stream was not passing through the body of the resin. The obvious result of this was that glycol losses were extremely high. By the end of the first stage calculated glycol losses were 29.2 g. This problem was made even worse because the distillate had to be collected in a conical flask rather than an open measuring cylinder and hence it was difficult to judge the rate of the reaction. This meant that more acid value tests than usual were carried out on this batch. Consequently, the total amount of resin removed for samples was calculated as a percentage of the initial charge and for the second stage of the reaction the maleic anhydride charge was reduced accordingly. Propylene glycol losses from the first stage were also made up before the start of stage 2.

Finally, it is worth noting that all of the batches of resin A produced during this experiment were of an acceptable colour although all were darker than batches normally produced on a production scale. It is felt that the practice of holding the resin overnight in the laboratory is the most significant cause for this. The most severe colour problems were experienced at the start of the second stage of the final batch. In this case the resin became very much darker following the charging of the maleic anhydride although this colour did fade significantly during processing. The deeper colour of this batch is thought to have occurred because of insufficient purging before the start of stage 2.

3.4.8 Conclusions of the Laboratory Investigation

(i) Polyester resins can be produced more quickly and with less glycol loss if the flowrate of inert gas is minimised.

(ii) A high inert gas flowrate makes the control of the reaction conditions difficult. This can result in high losses of propylene glycol.

(iii) It is necessary to sparge inert gas through the resin body during the later stages of the process to remove excess water.

(iv) It is possible to produce a polyester resin in an inert atmosphere without providing a continuous purge, although a slight deterioration of the resin colour may occur.

3.5 The Implementation of the Modified Purging Programme on the Manufacturing Process

The results of the laboratory-scale experiments into the effect of the purging programme on the manufacture of polyesters indicated that significant improvements could be achieved if modifications were made to the purging programme used on the production scale process. However, before trials could be carried out on the manufacturing process, it was necessary to purchase and install new nitrogen flow meters. The existing meters on all of the polyester reactors were found to be greatly over-sized and this made accurate control of the inert gas flowrate very difficult. Once the correctly sized meters had been installed ten batches of resin A were produced following the normal manufacturing instructions. In each case a modified purging programme was used. This involved turning off the inert gas flow to the still during the distillation stages of the process. The inert gas purge was reapplied to the dome of the reactor while the resin was cooling between stages. The second stage of resin A manufacture is carried out by the solvent process and this was left unchanged.

The investigation was also extended to include the production of a second resin, referred to as Resin B. Resin B is a frequently produced isophthalic based polyester both stages of which are produced by the fusion process, or more normally by the distillate reflux method when produced on the larger reactor. This resin was selected for use during this investigation because at the time of the investigation it was being produced more regularly than resin A and because very high rates of glycol loss were being experienced.

3.5.1 The Determination of Actual Glycol Losses

Before assessing the effect of the modified purging programme on the rate of loss of glycol from the process, it was necessary to accurately determine the actual glycol loss from the established process. This also served as a useful check on the method used to calculate the required in-process glycol additions which are made to account for the losses. In order to do this the distillate from the batch of resin of interest was diverted to a glass reinforced polyester (grp) tank. The tank was equipped with an air-operated agitator and a level indicator. The bulked distillate was sampled hourly during the distillation periods of the process. The tank level was also recorded. The two stages of the process were considered separately; consequently the tank was drained while the resin was being cooled for the maleic anhydride charge. The propylene glycol content of the distillate was determined from the density and refractive index of the sample. As with the laboratory work, an average value was used when the two methods did not agree. In this way it was possible to estimate the total volume of propylene glycol lost from the process during the course of a batch. In general, it was found that the agreement between the two methods was less good for samples taken during the second stage of the process. This was particularly true for Resin A where the second stage of the reaction is carried out by the solvent process.

Tables 3.2 and 3.3 show a summary of the results obtained for resins A and B respectively. In the case of resin A the colour of the final resin has also been given. The colour specification for resin A is 150 Hazen Units maximum. Resin B is an accelerated resin and hence the Hazen scale is not appropriate due to the purple colour of the accelerator. However, in some cases resin samples were collected before the addition of the accelerator and the colour determined. All these samples were found to be well within 150 Hazen Units.

Table 3.2 Actual Glycol Losses: Resin A - Reactor 6

Batch	Reaction Time (hrs)		Glycol Additions		Colour	Modified
Number	Stage 1	Stage 2	Total (kg)	% of Feed	(Hazen)	Purge ?
514-540	21.3	12.8	84	1.9	50-60	No
563	17.75	11	71	1.6	40-50	No
564	17.5	11.5	71	1.6	50-60	No
565	23	12.5	71	1.6	50-60	Yes
567	17	12.25	85	1.9	50-60	Yes
568	17.25	12	71	1.6	50-60	Yes

Table 3.3 Actual Glycol Losses: Resin B - Reactor 7

Batch	Reaction Time (hrs)		Glycol Losses		Glycol	Modified
Number	Stage 1	Stage 2	Total (kg)	% of Feed	Adds (kg)	Purge ?
176-197	16.9	9.6	Unknown	-	477	No
236	20.75	7.5	653	22.7	378	No
239	17	10.25	700	24.3	169	No
240	28	13	478	16.6	378	No
241	29.5	9.5	478	16.6	472	Yes
243	21.5	7.5	509	17.7	354	Yes
244	21.5	8.5	631	21.9	330	Yes
245	19	10.25	738	25.6	425	Yes
247	18	9.5	Unknown	-	472	Yes

3.5.2 Discussion of Production Scale Findings

It can be seen from the preceding tables that the significant improvements in the process efficiency obtained by minimising the inert gas purge rate in the laboratory scale experiments were not achieved on the production scale. However, table 3.2 shows that the colour of resin A is unaffected by the removal of the continuous nitrogen purge to the vapour space. The analysis of the distillate was stopped as soon as it became apparent that no significant improvements were being experienced although the purging programme was adopted since it was clear that the established high rates of flow were not necessary.

It was clearly disappointing to find that the successful results achieved in the laboratory had not been repeated on a production scale. A literature search was therefore carried out to determine why the overhead equipment on the large scale reactors was so inefficient. During this search a relationship was found which could be used to determine the minimum liquid flow rate which would be necessary to wet the column packing sufficiently to allow efficient mass transfer to take place(14). It was found that the liquid flowrate through the packed column on reactor 7 was too low by a factor of approximately 20. This work is discussed fully in chapter 5. As a result of this work it was decided that the major cause of the equipment inefficiency was the dry packing rather than the effect of the inert gas flow. Since it would be necessary to return very large quantities of water to the reactor in order to provide sufficient liquid to the existing columns this situation could only be resolved by redesigning the overhead equipment.

3.6 Conclusions

The laboratory investigation showed that it was possible to reduce the reaction time and the rate of loss of glycol from the reactor by eliminating the inert gas purge during the distillation stage of the process. This was shown to have a minimal effect on the colour of the final resin. However, when extended to the production scale, no detectable improvement was noted. This is thought to be due to the hydrodynamics of the packed column handling the vapours generated in the reactor. In spite of these disappointing results the modified purging programme was adopted on the polyester plant because it had no detrimental effect on the resin quality and represented a slight raw material saving and reduced the overall load on the effluent treatment plant.

CHAPTER 4

THE IMPORTANCE OF INERT GAS QUALITY IN THE MANUFACTURE OF UNSATURATED POLYESTERS

CHAPTER 4

THE IMPORTANCE OF INERT GAS QUALITY IN THE MANUFACTURE OF UNSATURATED POLYESTERS

4.1 Introduction

At present cryogenic nitrogen is used to provide an inert atmosphere for commercial polyester manufacture as described in section 3.3. However, for many other applications within the factory where an inert gas is required, the nitrogen produced by the Pressure Swing Adsorber is of an acceptable quality. Cryogenic nitrogen is extremely expensive and the storage facilities take up a large amount of valuable site space: significant cost savings would therefore be available if polyesters could be produced in an environment containing two per cent oxygen by volume, such as that currently obtained by PSA methods.

Very early work on polyester technology had indicated that the inert gas should have an oxygen content of not more than 0.02% by volume(11). However, the same source also recommended an inert gas flowrate which is equivalent to a rate up to forty times greater than that currently used in commercial production. In addition, this very high flowrate was sparged through the resin mixture at all times. It was felt that the very high purity of the gas quoted may be as a result of the very high degree of contact between the inert gas and the reacting resin. If this was the case, a lower grade of inert gas may be acceptable in the modern manufacturing process, particularly as the development of glycol-water separation equipment has reduced the likelihood of oxygen entering the system through the vent. A series of experiments was carried out to determine the acceptability of lower quality inert gas for the laboratory scale manufacture of various grades of resin. The work was carried out in two parts. Firstly, a selection of resins to represent the range of products was made. When this work appeared successful, a second, more detailed investigation was carried out on resin C. Resin C is produced with a very high proportion of maleic anhydride and hence is highly reactive during the cross-linking reaction with styrene. As shown in equation 3.1, the presence of oxygen destroys some of the unsaturated bonds and hence adversely affects the reactivity of the resin. In addition, resin C has a tight product specification for molecular size distribution which is determined by gas permeation chromatography. GPC analysis of the resins produced in an atmosphere of 'PSA grade' nitrogen would therefore highlight any differences in the chemical structure of the resin which may not be clear from the physical properties alone.

4.2 Selection of Resins for Investigation

The polyester plant produces a large number of different resins for a variety of applications. It is important that any grade of nitrogen used for purging the reactors should be suitable for use on any of the resins produced on the plant. There are two reasons for this. Firstly, reference to the economic case given in Appendix A shows that the fixed rental and service charges make up a significant proportion of the total cost of the cryogenic nitrogen system. Consequently, savings would be dramatically reduced if the system had to be retained for the production of only one or two resins. Secondly, confusion would be likely to occur on the plant if one set of nitrogen lines was used for some resins and a second set was required for other resins.

Since it was impractical to investigate each resin, three resins were selected which were considered to represent the resin range. These consisted of a single stage orthophthalic resin, referred to as resin D; a two-stage isophthalic resin produced by the fusion process, resin E; and a fully unsaturated polyester which will be known as resin F. Resin D is manufactured by the solvent process and its end use means that the molecular size distribution must be within specified limits. This is checked by performing GPC on a sample of the final resin. By selecting this resin for investigation it was possible to determine whether the chemical structure of the resin was being affected in a way which could not be detected by the physical properties alone. Resin E is a very reactive resin produced for moulding applications. In particular, it was selected because it is used in the manufacture of white products. Consequently, it is important that this resin retains a good colour. Resin F is unusual in that it contains no saturated acid. It is not made regularly on the plant, but was selected because it had been reported that batches previously produced in the laboratory had formed a skin on exposure to air and hence the resin had shown itself to be particularly sensitive to oxygen.

4.3 Equipment

All batches were produced on a two litre scale using standard laboratory equipment, shown in figure 4.1. A small packed column was used with a reflux condenser to control the column top temperature and hence reduce the loss of glycol from the reactor.

4.4 Experimental Procedures

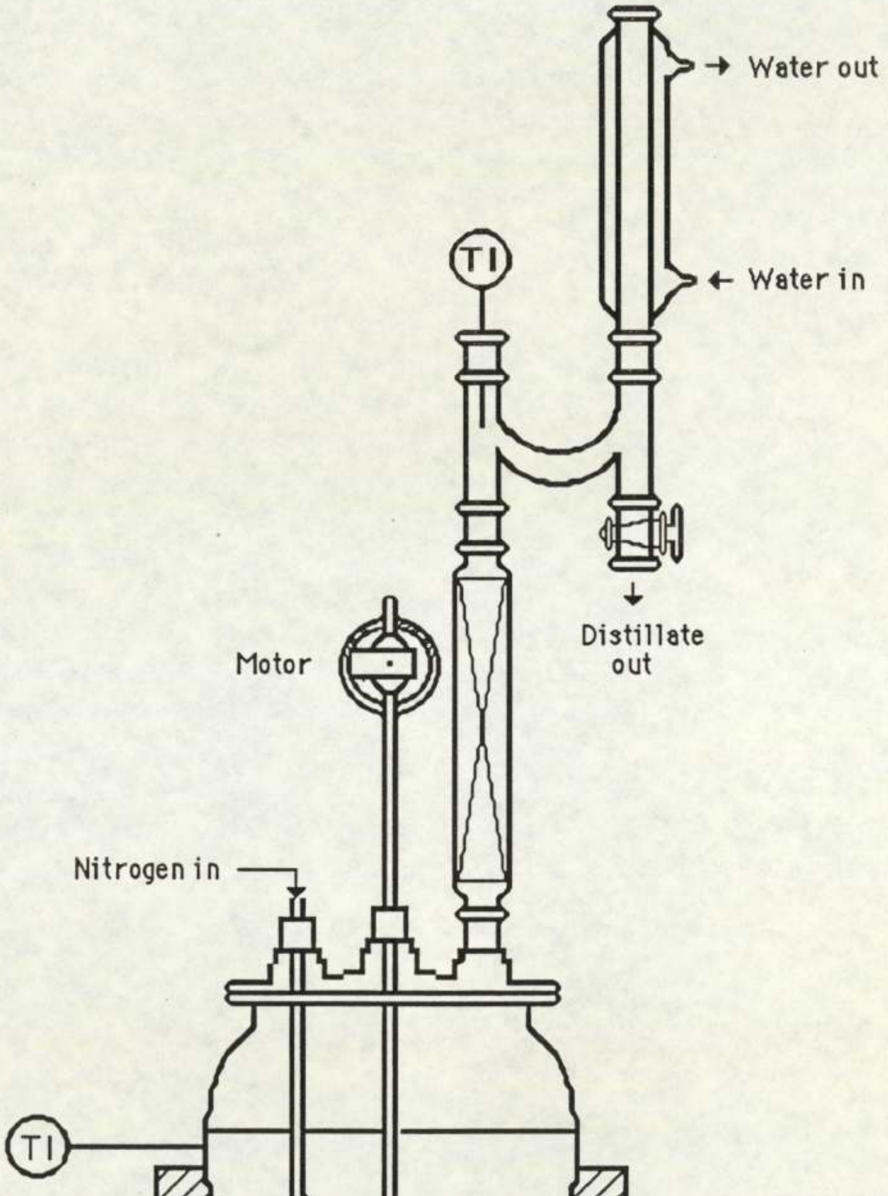
Each of the resins selected for initial investigation were produced following the procedures described in the appropriate provisional manufacturing instructions. This made it possible to make comparisons between batches made using nitrogen containing three per cent oxygen (henceforth referred to as PSA nitrogen) and those made in the laboratory using 'white spot' nitrogen. It is standard practice in the laboratory to produce all polyester resins by the fusion process since adequate control of the column top conditions can be maintained more easily than is possible in the plant with current equipment. On a production scale resin D and the second stage of resin E would normally be produced by the solvent process. It was felt it was acceptable to use the fusion process for these trials because it would represent a worse case than the solvent process since the presence of xylol vapour would itself act as an inerting agent. In addition, it was felt that comparison with previous laboratory batches would be more relevant than the manufacturing scale batches because of other differences in the process and the equipment. In all cases the purging programme developed in chapter 3 was adopted, ie no nitrogen flow during the distillation stage except as an aid to water removal at the end of the process. It should be noted that it has been found that severe discolouration of polyester resins can occur when the resin is cooled and left overnight during processing. For this reason a small bleed of high purity 'white spot' nitrogen was passed across the top of the resin mixture overnight.

4.5 Observations and Results of Initial Trial Batches

4.5.1 Resin F

Resin F is produced without the use of a saturated dicarboxylic acid to increase the chain length. As mentioned in Section 4.2, previous work in the laboratory has shown that contact with air during the taking of samples for process tests

Figure 4.1 Standard Laboratory Equipment for the Manufacture of Polyester Resins



has resulted in the formation of a skin on the surface of the resin. This has not been found to be a problem on the polyester plant where samples are taken from the bottom of the reactor and air is not introduced into the reactor environment. In order to minimise the formation of the skin, resins produced in the laboratory are charged with a small quantity of hydroquinone at the start of the reaction.

The batch of resin F produced with a PSA nitrogen purge was made by the process described in the provisional manufacturing instructions. The reaction proceeded more quickly than is normally the case for a polyester. This is because diethylene glycol has a much higher boiling point than the propylene glycol more normally used in polyester manufacture. Therefore, the rate of increase of reactor temperature need not be so carefully controlled to avoid glycol losses and the reactor top temperature can be more quickly attained.

The resin was produced without problem until the final process test was taken. It was found that a skin had formed around the thermometer pocket and the agitator shaft during the twenty minute period between taking the final test and turning off the heat. The quantity of skin formed was not felt to be an undue problem and could be further controlled by increasing the hydroquinone charge slightly without having an effect on the final properties of the resin.

4.5.2 Resin D

Resin D is manufactured by the solvent process. The first batch produced in the laboratory using PSA nitrogen was made using the formulation described in the provisional manufacturing instructions. The reaction proceeded without problem although it was noticed that the resin became significantly darker when the resin was cooled for blending. It was also noticed that the acid value of the resin dropped quickly at the end of the reaction. This resulted in a final resin with an acid value of 15.6 mg KOH/g compared with a product specification lower acid value limit of 16mg KOH/g. However, the resin viscosity, density and solids were all in balance and a sample was submitted for analysis by GPC. The plot of the molecular size distribution is shown in figure 4.2. It can be seen that there is a wider spread of molecular sizes in the resin produced with a PSA nitrogen purge when compared with a standard laboratory produced batch, figure 4.3. The maximum of the peak has been shifted slightly towards the higher molecular sizes but this cannot be directly related to a mean molecular size. The most significant deviation from the standard plot is the appearance of a secondary peak at the high molecular size end of the plot. This indicates a higher degree of condensation than normal, or possibly some crosslinking. The presence of this peak on the gpc plot would make the resin unacceptable for its end use. The plot was then compared with a selection of GPC plots from batches produced on the plant. It was found that the plot achieved in the laboratory was almost identical to some of those from the earliest full-scale batches produced on the works. The problem had been corrected by increasing the glycol excess. It was decided, therefore, that a second batch of resin D should be produced in the laboratory, purging with PSA nitrogen and using the formulation currently used on the works.

The second batch produced in the laboratory was successfully completed. The reaction was stopped slightly earlier than the first batch to ensure that the final acid value was within the specification. Table 4.1 below shows a summary of the final resin properties of both batches.

Table 4.1: Final Properties of Resin D Purged with PSA Nitrogen

	Acid Value (mg KOH/g)	PRS Viscosity (25°C)	Density (g/cm^3) (25°C)	Solids Content (%)
Specification	16.20	10A-12	1.102-1.148	64-67
Batch 1	15.6	10A	1.1254	65.3
Batch 2	17.9	9A-10	1.1183	66.5

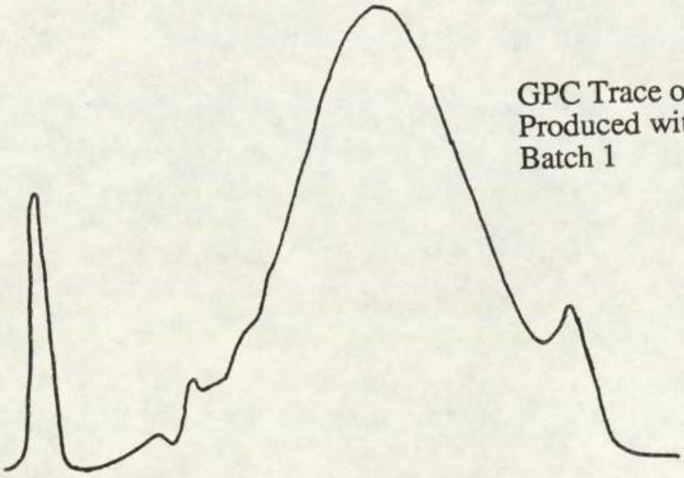


Figure 4.2

GPC Trace of Resin D
Produced with PSA Grade Nitrogen
Batch 1

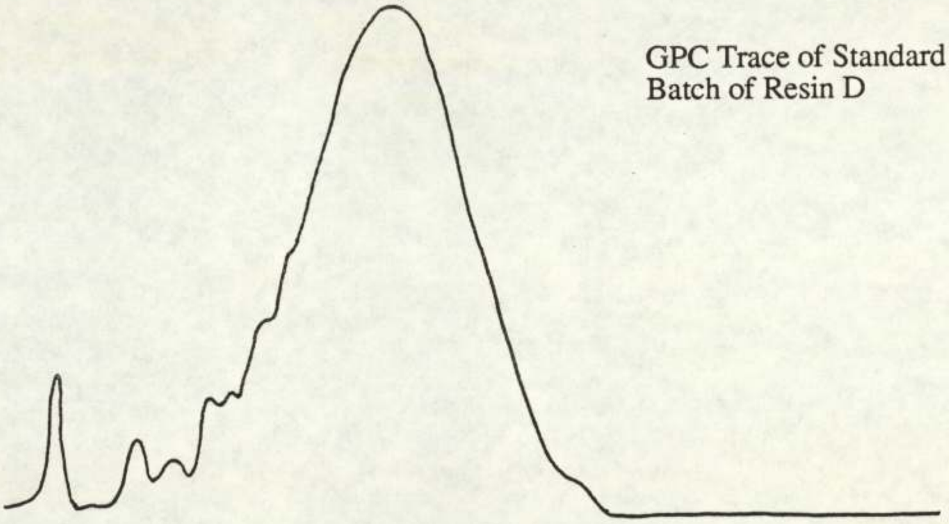


Figure 4.3

GPC Trace of Standard Laboratory
Batch of Resin D

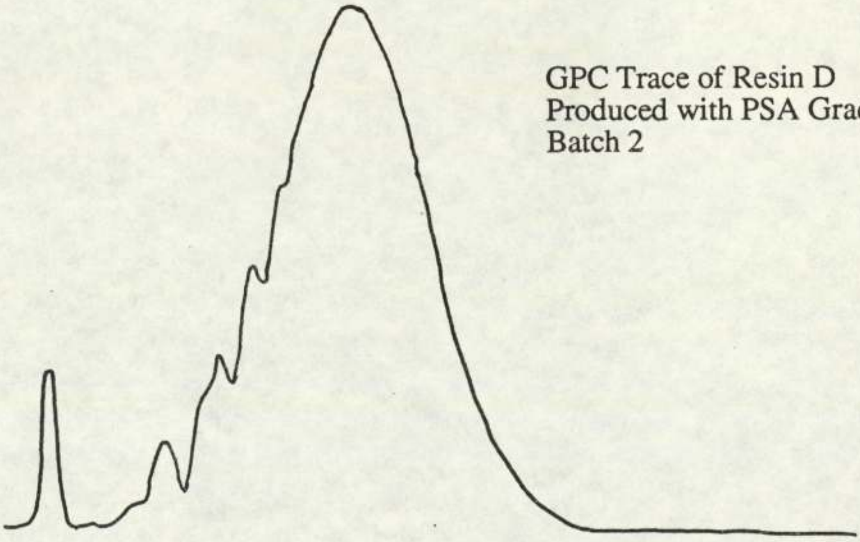


Figure 4.4

GPC Trace of Resin D
Produced with PSA Grade Nitrogen
Batch 2

It can be seen from the results above that the second batch produced a final resin with a lower viscosity together with a higher solids content. This suggests that the resin is less highly condensed than the first batch. The GPC trace which is shown in figure 4.4 confirms that the resin is less condensed. The secondary high molecular peak which was apparent in the first batch is not present in the second resin. Instead, there are several peaks on the lower molecular size side of the graph. These are low molecular weight oligomers and their presence implies that in this instance the glycol excess was too large resulting in the formation of more molecules of low molecular weight rather than fewer molecules of higher molecular weight. The presence of these peaks does not affect the suitability of the resin for its end use - although it is obviously undesirable to add more glycol than is necessary to a resin and further work would be necessary to ascertain the optimum glycol charge. However, since glycol losses differ greatly between the plant and the laboratory, this work should be carried out on the works scale. Once this has been completed this resin could be produced on a works scale with a PSA nitrogen purge.

4.5.3 Resin E

Resin E is a two-stage isophthalic polyester resin which is used in moulding applications. It is a very reactive resin because it has a very high proportion of unsaturated acid in its formulation. It was felt that this high degree of unsaturation would highlight any problems caused by the presence of the PSA nitrogen. It is also particularly important that this resin displays a good final colour.

The first stage of the reaction proceeded without problem and the colour of the resin remained good. The second stage of the reaction started well but it was noticed that the rate of removal of water dropped very quickly during the second stage. Early in-process tests proved inconclusive as the provisional manufacturing instructions gave PRS viscosity values for tests carried out at 80% solids and it was found that the resin did not remain clear at such a high solids content and the bubble in the PRS tubes could not be clearly seen. It was decided, therefore, to compare the laboratory results with the results of in-process tests carried out on the plant at 66% solids. The viscosity specification for resin E is 9A-10A PRS at 66% solids and 25^{o}C. The first viscosity test carried out at 66% solids gave a PRS viscosity of 11A. The corresponding acid value for this sample was 93 mg KOH/g resin. These results were well outside the acid value specification of 30-35 mg KOH/g resin. Consequently, the batch was abandoned.

A second batch of resin E was then produced to ensure that there had not been some error which could explain the results described above. Two minor changes were made to the process. Firstly, the maleic anhydride charge was reduced slightly to allow for resin removed from the reactor for process testing in the first stage. Secondly, every effort was made to remove as much water from the resin as quickly as possible in an attempt to bring the acid value down to within the specification limits. Therefore, the agitator speed was increased and the PSA nitrogen was sparged through the resin earlier and at a higher rate. This was successful in increasing the rate of removal of water, and the resin appeared to be reacting normally. However, the viscosity then began to increase rapidly and again it was necessary to stop the resin. The final properties of the resin were an acid value of 46.1 mg KOH/g resin and a PRS viscosity of 13A.

Resin E was the first resin to indicate that the PSA nitrogen may be affecting the chemistry as well as the colour of the resin. It was felt that the effects of the oxygen in the inert gas may be reduced by processing the second stage of the resin by the solvent process because water is more easily removed by the azeotrope and less sparging is required until the very end of the process. It was suspected that the addition reaction shown in equation 3.1 was occuring. Turunen(13) found that this side-reaction follows a free-radical polymerisation mechanism. It is known that the free-radical reactions can be initiated by the presence of molecular oxygen and this could explain the increased viscosity of resin E produced in the laboratory. However, the curing reaction also has a free-radical mechanism and if this is the mechanism for the above side reaction, the reaction can be prevented by the inhibitors used to prevent premature gellation of the resin. It was decided to follow up this theory by running a second set of experiments where the effects of charging hydroquinone at the start of the reaction could be investigated.

For this second set of experiments a different resin, Resin C was selected for investigation. There were several reasons for this. Firstly, the resin E experiments had shown that the effects of the increased oxygen content were made more noticeable when the resin is more highly condensed. Resin C is a very highly condensed product, and in fact is processed to within 5 points of its acid value gel point. In addition, resin C is produced for food use applications and as such only a small quantity of volatile components can be present in the final resin. This means that the solvent process cannot be considered in this case. It also means that only very minor changes in the glycol charge can be considered. Finally, like resin D, a product with an acceptable GPC profile must be obtained and this makes it possible to compare experimental batches with earlier laboratory batches and with works batches.

4.6 PSA Nitrogen in the Presence of Hydroquinone

4.6.1 Introduction

It has already been explained that resin C is a very highly condensed and highly reactive resin in which only a low proportion of volatile components can be present. Not only must each batch of resin meet the physical specification, it must also have an acceptable molecular size distribution as shown by gel permeation chromatography. Because of the nature of this resin it would be almost impossible to make any significant changes to either the formulation or the manufacturing process. It was felt, therefore, that if resin C could be successfully produced using PSA nitrogen, all other polyester resins could also be produced in this way. This investigation was intended to prove conclusively whether PSA nitrogen could be used in the manufacture of polyesters and it was necessary to be sure that any variations in the final properties of the resin were due to the presence of oxygen in the inert gas rather than variations in raw materials or resin-making technique. For this reason a control batch of resin C was also produced by an identical process using the same batches of raw materials.

4.6.2 Experimental Method

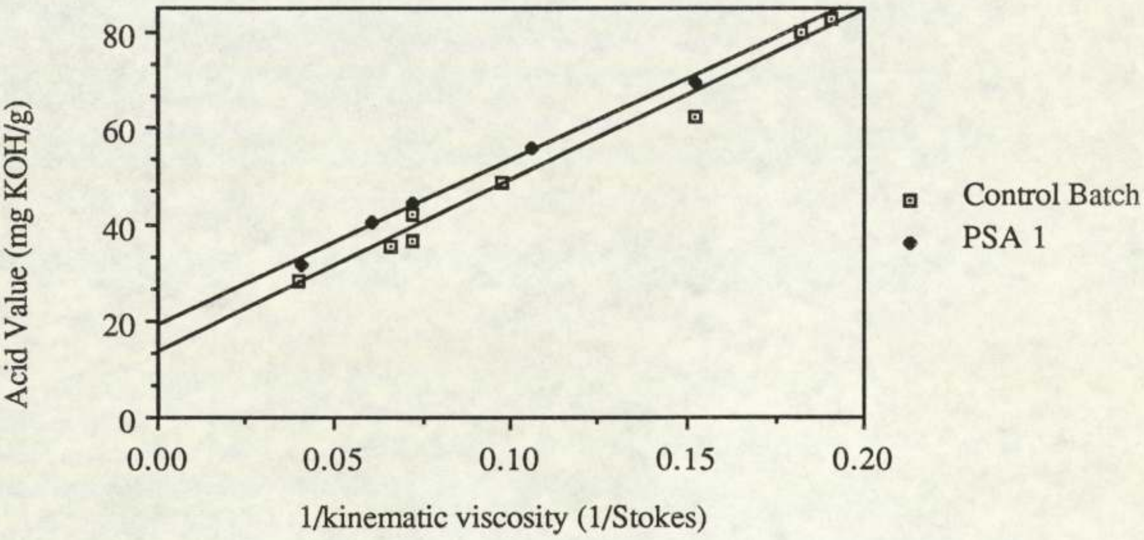
Resin C is produced by a single stage fusion process following the procedure described in the provisional manufacturing instructions. The formulation for the resin is the same in the laboratory and on the works for the reasons already given. This formulation was, therefore, used in these experimental batches with an addition of 200 ppm hydroquinone which was added to the reactor with the acids. This inhibitor concentration was selected because it was felt to be the maximum which could be accepted in the final product when the inhibitor added prior to blending is also taken into account. It is not possible to add all the hydroquinone at the start of the reaction because some decomposition occurs during the reaction process and it is necessary to ensure that sufficient inhibitor is present at the start of the blending process to prevent gellation of the resin. If the PSA nitrogen was found to produce a resin which met the product specification apart from the gel time, further work would be carried out to determine the optimum hydroquinone charge.

In order to make as many direct comparisons as possible the control batch and the first batch of resin C produced with PSA nitrogen were run in parallel. However, because it is not possible to blend two resins at the same time, the resin charge times were staggered by four hours in an attempt to ensure a similar time span between blending times.

4.6.3 Results

In the early stages of the resin manufacture there were no noticeable differences between the two resins. On the second day of the reaction it was noticed that the control resin was much slower to start distilling while the PSA nitrogen resin was reacting quickly. This was thought to be because the PSA nitrogen resin had not reacted far the previous day and hence had a higher concentration of the unreacted raw materials. However, the PSA nitrogen resin continued to react faster than the control resin and reached the process end point before the control resin even though it was started later. It was also found that the PSA nitrogen resin had a higher viscosity for a given acid value than the control resin especially towards the end of the process. However, both resins were within the process limits when the reaction was stopped. The variations in the processing of the two resins can be more clearly seen by referring to the graph of acid value vs reciprocal solution viscosity shown in figure 4.5.

Figure 4.5 Acid value vs Reciprocal Viscosity



It was when the resins were blended that the real differences became apparent. Although both resins were blended to a similar solids content, the PSA nitrogen resin was found to have a significantly higher viscosity. A full summary of the properties of both resins is provided in Table 4.2.

Table 4.2: Properties of Experimental Batches of Resin C

	PRS Viscosity (70% solids)	Melt Viscosity @ 140°C	Gel Time (mins)	Acid Value (mgKOH/g)	Ferranti-Shirley Viscosity (Poise)	Solids Content (%)	Density (g/cm^3)
Control Resin	14-	11	15.9	26.7	6.9	62.4	1.1109
PSA Nitrogen	13A-14	16	10.5	30	19.2	62.4	1.1103

It can be seen from the table that the most significant variation between the two resins is the viscosity of the final blended resin. This implies that something happened between the taking of the last process test and the end of the blending process which caused the viscosity of the PSA nitrogen resin to increase.

Samples of both resins were also analysed by gel permeation chromatography and the molecular size distribution profiles are shown in figures 4.6 - 4.8 along with the profile of a standard resin. Resin C, unlike resin D should have a secondary peak at the high molecular size end of the profile. The control resin profile has the correct general shape but is slightly undercondensed. It is felt that if the resin had been allowed to react for a further hour or two, the correct profile may have been achieved. The PSA nitrogen resin molecular size distribution profile is totally unacceptable. The secondary peak is extended along the molecular size axis which means that some molecules had molecular sizes far in excess of the maximum permissible.

It was felt that the blending process was most likely to be the cause of the problem and two more batches were planned. Reference to Table 4.2 shows that the PSA nitrogen resin has a significantly shorter gel time than the control batch. Whilst the gel time cannot be directly related to the concentration of inhibitor present in the resin, the significant reduction in gel time suggests that a large proportion of the hydroquinone added at the beginning of the reaction was used up during the reaction stage. It was decided to run a further two batches of resin C produced with PSA nitrogen. The first batch had the same quantity of hydroquinone added on blending (80 ppm) but the blending temperature would be reduced from 150°C to 130°C. The second batch would be blended at 150°C like the first two batches but the hydroquinone concentration would be increased to 150 ppm.

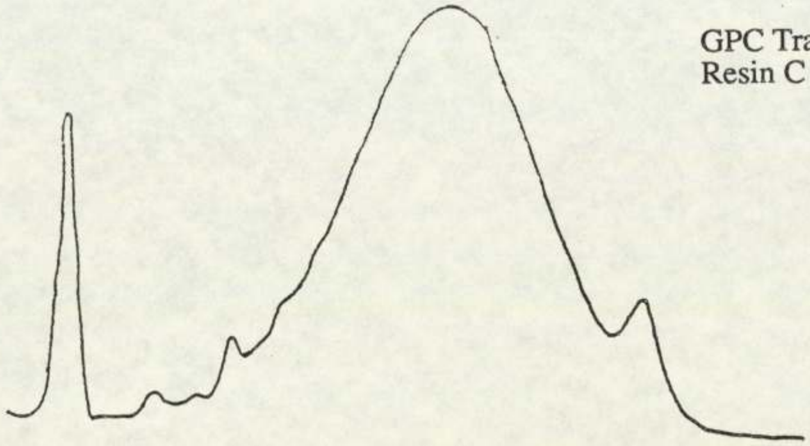


Figure 4.6

GPC Trace of Control Batch of Resin C

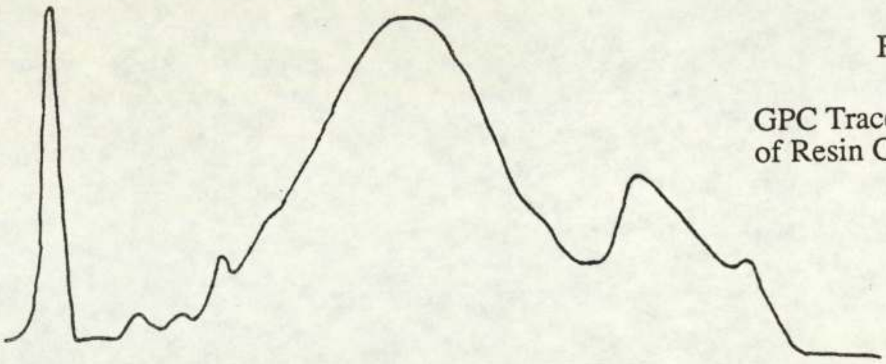


Figure 4.7

GPC Trace of PSA Batch 1 of Resin C

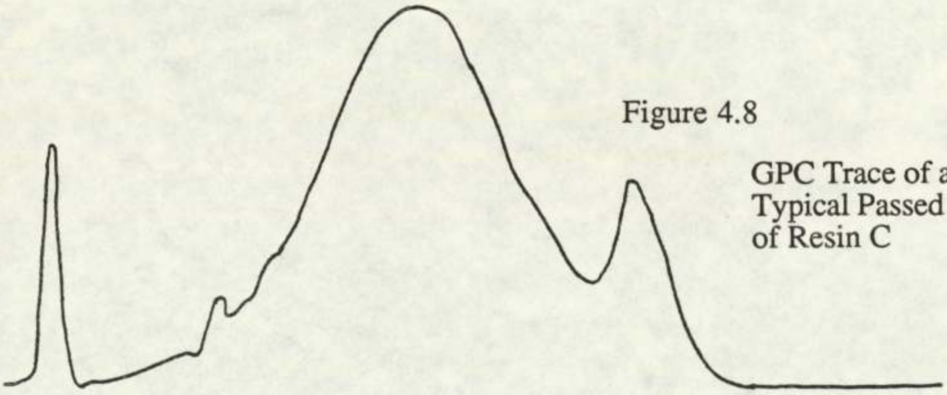


Figure 4.8

GPC Trace of a Typical Passed Batch of Resin C

4.6.4 The Blending Process

Both of the additional batches of resin C were produced from the same formulation as the initial batches, including the 200 ppm hydroquinone, and processed in the same way. The differences in the resin production came at the blending stage. The first of the batches was cooled to a temperature of 130°C before blending, and a further 80 ppm hydroquinone was added to the styrene. This batch will be referred to as PSA batch 2. The second of these resins was cooled to 150°C for blending but the hydroquinone addition was increased to 150 ppm. This is PSA batch 3. Both resins reacted normally although it was noticed that PSA batch 3 was more viscous than PSA batch 2 and, in fact, the final PRS viscosity was slightly above the processing specification of 14-14A. Reference to the Acid Value vs Reciprocal Viscosity graph in figure 4.9 shows that the gel point acid value for this batch was found to be 24 mg KOH/g resin whereas the other two batches produced with PSA nitrogen had a gel point acid value of 18-19 mg KOH/g resin. The reason for this is uncertain but the PSA nitrogen sparge was introduced into PSA batch 3 two hours after PSA batch 2. PSA batch 3 was also found to have a reaction time two and a half hours longer than PSA batch 2. It is felt that this extended reaction time may have increased the opportunity for the production of molecules of very high molecular size and hence increased the viscosity of the resins.

Figure 4.9 Acid value vs Reciprocal Viscosity

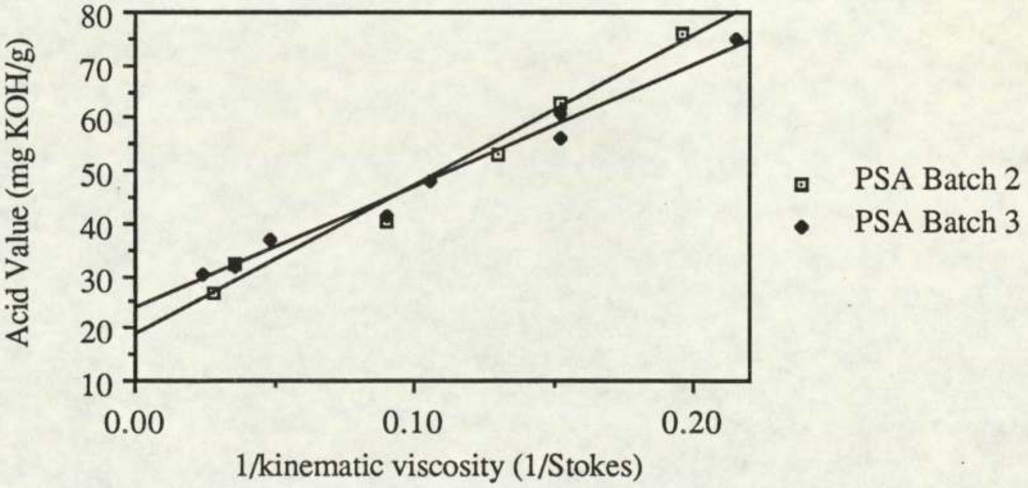


Table 4.3 gives a summary of the properties of PSA batches 2 and 3. Both resins are again found to have a much higher viscosity than the specification. Samples of these resins were not submitted for GPC analysis because the high viscosity of the first PSA resin had made cleaning of the columns difficult.

Table 4.3: Properties of PSA Batches 2 and 3

	PRS Viscosity (70% SRY)	Melt Viscosity @ 140°C	Acid Value (mg KOH/g)	Ferranti-Shirley Viscosity (poise)	Solids (%)	Density g/cm^3
PSA 2	14A	20	26.6	24.7	61.0	1.1082
PSA 3	15-	20.5	30.2	27.8	62.4	1.1119

The table shows that in spite of the differences between the two resins during processing, the final properties of the resins are similar. The viscosity and the density of PSA batch 2 are lower than PSA batch 3, but this is in balance with the lower solids content of the final blended resin. Once again it appears that the viscosity has increased on blending. However, the resin samples must be blended with styrene to give the PRS viscosity results and no problems had been noticed at this stage. This suggested, therefore, that the problem may be caused by the blending process. When a sample is blended for the PRS viscosity process test, the sample is removed from the reactor and weighed. The required quantity of styrene is then calculated before the resin is blended. During this time the resin has cooled considerably below the 130°C at which blending of PSA batch 2 took place. It was decided that one further batch of resin C should be produced. In this case, a larger batch (5 litres) would be produced by the same process as the other resins. However, once the resin had reached the process end point specification, half of the batch would be removed and cooled. The remaining half would be hot blended in the same way as the previous resins. Once the solid resin has completely cooled it would be broken up and charged slowly to styrene until the correct solids content was achieved. The temperature of this blending process would be controlled to ensure that it did not exceed 65°C, the temperature at which blending takes place on the works.

The charge for the standard 2 litre batch used in the previous experiments was multiplied by a factor of 2.5 to give the 5 litre charge. The packed column and the condenser size were not changed. This was not considered to be necessary as the available overhead equipment was already much larger than the equivalent on the works scale. The resin proceeded normally at the start of the reaction. However, it was noticed that the resin began to thicken rapidly later on. The last process test taken showed an acid value of 35 mg KOH/g resin and a PRS viscosity of 18-18A. Within ten minutes of this sample being taken the resin began to gel in the reactor. Immediately the heat was turned off and the reaction was stopped by adding glycol to the reactor. The reason why this batch should gel while the two litre batches did not do so was uncertain. However, the larger agitator for the five litre reactor appeared to be more effective than on the two litre scale. This meant that a deep vortex was created and hence a larger proportional surface area was in contact with the oxygen in the PSA nitrogen. The increased reaction time also meant that more samples were taken for process testing and hence there were more opportunities for additional oxygen to enter the system.

4.6.5 Conclusions

The gellation of the 5 litre batch of resin C makes it impossible to use PSA nitrogen on a works scale. Although some of the other resins were produced successfully, it cannot be used on a production scale reactor if there is the slightest risk of gellation. Also, it is not economically viable to use different grades of inert gas for different resins on a multi-purpose plant. However, this investigation does indicate that PSA-grade nitrogen may be safely used in the manufacture of certain polyester resins. This means that in the event of the cryogenic nitrogen system failing or running out, it is possible to continue with the manufacture of selected resins.

Finally, the results of this should not prevent the investigation of any other economic sources of inert gas which may become available in the future. Trials carried out on a reactive, highly condensed polyester resin may well indicate the maximum permissible concentration of oxygen which may be acceptable in an inert gas for use on the polyester reactors.

CHAPTER 5

THE DETERMINATION OF OPTIMUM OPERATING CONDITIONS FOR OVERHEAD EQUIPMENT

CHAPTER 5

THE DETERMINATION OF OPTIMUM OPERATING CONDITIONS FOR OVERHEAD EQUIPMENT

5.1 Introduction

Before it is possible to produce the most effective design of the overhead equipment, it is necessary to establish necessary operating conditions and estimate the relevant flowrates and compositions. This chapter describes the work carried out to evolve the relevant information and also the various techniques used to cross check the results before carrying out the design calculations.

5.2 Estimation of Vapour Flowrates and Composition

In order to correctly size the overhead system required for a reactor it is necessary to have an idea of the likely throughput of such a system. Initial work was carried out in the laboratory to determine a mass balance for the polyesterification reaction and, by making no attempt to separate the glycol from the distillate, to estimate a vapour loading for the condenser. These results were then scaled up to the production scale to give an indication of the order of magnitude of the vapour flow through the full scale equipment. However, it would be inappropriate to base a design on data which has been scaled up by a factor of over five hundred. For this reason, it was decided to estimate these flowrates by two other methods. Firstly, the rate of flow of vapour from the full scale equipment was estimated from the rate of removal of distillate from resin manufacture. Secondly, a mass balance was carried out by assuming compositions based on the vapour liquid equilibrium data. Refer to figure 6.1.

5.2.1 Laboratory Determination of Vapour Flowrate

The initial work to determine the vapour flowrates and composition was carried out in the laboratory to enable a mass balance on the process to be carried out. In addition, it was possible in the laboratory to modify the process to enable the actual composition of the vapour leaving the reactor to be determined by not attempting to separate the propylene glycol and water fractions of the distillate. To carry out an accurate mass balance on the production scale would be almost impossible because there was no way of accurately measuring some critical parameters such as rate of removal of distillate from the reactor. In many cases it is not possible to accurately determine the final resin yield particularly when the resin is transferred to a blender for further processing.

In order to gain some idea of the loading on the overhead equipment and the typical composition of the vapour leaving the reactor it was decided to pass the vapour directly into a total condenser and to collect everything produced from the reactor. This distillate was collected at intervals, analysed for glycol content and make up glycol was added to the reactor. Resin A was chosen for this experiment because the formulation contains a single glycol and hence analysis of the distillate was simplified. The analysis was carried out on a half-hourly basis and the refractive index and density of a distillate sample was determined. Because of concern about the effect of unknown impurities on these methods, the percentage of glycol lost was assumed to be the average of the results given by the two methods.

When resin A is made on the plant the second stage of the process uses the solvent method although the fusion method is normally adopted in the laboratory. For this reason it was decided to make a 10 litre batch for the first stage and to split this into two 5-litre batches for the second stage, one to be run by the fusion process and one by the solvent process. The nitrogen flow was set at the normal operating rate for laboratory scale manufacture, ie 3 cm^3/s. The first stage of the reaction showed good agreement between the calculated water product and that actually collected. However, in both second stages the quantity of water distilled off was considerably less than the theoretical based on the final resin acid value. Both final products were out of specification being too viscous for the final acid value. This is believed to have been caused by the delay in returning propylene glycol to the reactor resulting in an overcondensed resin. However, since the highest vapour flowrates were experienced during the first stage of the reaction these findings did not affect the required flowrate calculations. Therefore the experiments were not repeated.

Since it is not possible to measure the vapour flowrates in the overhead equipment it is necessary to estimate them based on the flowrates of distillate calculated from the laboratory experiments. The vapour flowrate can be considered to be a function of the size of the reactor charge, but it will also depend upon the heat flux into the reactor. In the laboratory this flux varied tremendously since it was the only means of controlling the system in the absence of a reflux but on the plant very sudden changes are not anticipated. All design calculations will be based on the highest flowrate determined in the laboratory. This will be scaled-up in relation to the batch sizes. Table 5.1 gives the scale-up factors for the charge sizes and flowrates. Table 5.2 gives an indication of the relative heat transfer areas for the three systems. Two values are given for the partial condenser heat transfer area to allow for the fact that the partial condenser has a larger diameter than the packed section beneath it. It is possible that the vapour does not enter the outer tubes of the heat exchanger under certain conditions.

Table 5.1 Polyester Manufacturing Equipment - Scale Factors

Batch	Unsaturated acid charge	Scale factor	Worst-case vapour flowrate	Nitrogen Flowrate	Mass % Nitrogen in vapour
10 litre	2200g	0.001	31.38g/min*	0.210g/min	13%
React 6	1630kg	1	61.35 kg/hr	3.956 kg/hr	6%
React 7	3260kg	2	122.69kg/hr	3.956 kg/hr	3%

* Composition of vapour at that flowrate, 7% glycol, 93% water by mass

Table 5.2 Heat Transfer Equipment

Reactor	Heat Transfer Area of Reactor Jacket	Heat Transfer Area of Partial Condenser	Scale Factor
10 litre	na	estimate 120cm^2	1/1039
Reactor 6	11.24m^2	** 12.47m^2 *** 5.24m^2	1 1/2.4
Reactor 7	18.38m^2	na	

based on average vapour density of 0.4 g/dm^3

** assumes vapour distributes ideally between all tubes after leaving packed section

*** assumes vapour does not expand on leaving packed section and hence uses only those tubes in the centre of the bundle.

5.2.2 Vapour Loading Calculations Based on the Rate of Collection of Distillate

In order to estimate the actual rate of distillation from the production reactors, it was arranged for the distillate to be measured from a number of batches produced on Reactors 6 and 7. This was achieved by timing the removal of a fixed weight of distillate. Samples of the distillate were then taken and the glycol content determined. It was then possible to use this information to estimate the vapour flow through the partial condenser and packed section for Reactor 6. It was also possible to estimate values for the packed column on Reactor 7 provided a constant level was assumed in the balance tank. Calculations for the greatest distillation rates are detailed in Appendix B. The maximum rate recorded on Reactor 6 was obtained from a batch of resin A when a rate of 37 kg/hr was achieved. However, it is important to note that this rate only takes account of distillate collected and internal reflux created by the partial condenser is not accounted for. This distillate consisted of 21% by mass propylene glycol. For Reactor 7 a rate of 301 kg/hr was achieved for distillate containing 37% by mass propylene glycol.

5.2.3 Mass balance calculation based on vapour liquid equilibrium data

It was attempted to complete a mass balance on the Reactor 6 overhead system based on the composition of samples collected and the calculated composition of the vapour stream from the vapour pressure data. The calculations were based on resin A because the first stage has only two raw material components and because there is a very large excess of propylene glycol present. The batch selected for analysis was number 566. It was attempted to estimate the flowrates at the beginning of the stage because it is easier to estimate the composition at this time and because the rate of evolution of water is greatest. An estimated vapour rate of 115.33 kg/hr was achieved. See Appendix C for the calculations.

5.3 The Effect of Column Top Temperature on the Manufacture of Polyester Resins

5.3.1 Introduction

A series of experiments were carried out in the laboratory to investigate the effect of varying column top temperature on the rate of reaction and the loss of glycol on the first stage of the production of resin A. The objective of this experiment was to determine optimum operating conditions for the resin. Only the first stage of the reaction was considered because the work carried out in the laboratory had already shown that glycol losses are greatest at this point because of the large excess of unreacted glycol present. Resin A was again selected for investigation because of the very high glycol excess.

5.3.2 Method

The resin was manufactured in a 2-litre reactor in the laboratory. Because it is not possible to accurately simulate the scale of the plant equipment in the laboratory, it was decided that the operation of a partial condenser would not be attempted. Instead the standard laboratory equipment with a short, well-lagged packed column was used as shown in Figure 4.1. Five runs were completed with the column top temperature ranging from 100°C to 140°C. The same charge was used for each batch and in each case the resin was processed to an acid value of approximately 10 mg KOH/g. The total distillation time was noted for each batch. Variations in heat-up time were not included although a higher permissible column top temperature does mean that a faster heat-up rate can be used. Distillate was collected at regular intervals and analysed using density and refractive index. It was extremely difficult to maintain a constant head temperature and so a 5°C margin was permitted for each run. This meant that if a column top temperature of 110°C was being investigated all distillate generated below a top temperature of 115°C would be collected. If at any time the column top temperature went above 115°C all distillate was refluxed or returned to the reactor and the rate of heat reduced until the column top temperature fell to the required value.

5.3.3 Results

During each batch plots were drawn showing the reactor and column top temperatures, the rate of distillate collection and the rate of loss of glycol. The final results are tabulated in Table 5.3 .

Table 5.3 Effect of Column Top Temperature on Reaction Time and Glycol Loss

Run No	Column Top Temp (°C)	Reaction Time (hrs)	Glycol Lost (g)	Glycol Lost (% of charge)
1	100	9.0	1.21	0.1
2	110	6.75	1.53	0.2
3	120	6.0	7.67	1.3
4	130	6.0	14.59	2.6
5	140	6.0	19.90	3.6

5.3.4 Discussion

These results clearly show that the rate of loss of propylene glycol rapidly increases with an increase in the column top temperature. It can also be seen that up to a column top temperature of 120°C an increase in the column top temperature reduces the reaction time. It was found that as the column top temperature increased it became more and more difficult to hold the temperature constant. Consequently, these temperatures were approached slowly and constant control of the heater was required to avoid overshooting. The column top and reactor temperatures also dropped significantly whenever a process test was carried out and some time was needed before the required conditions could be restored. These factors help to explain why the glycol losses were less than those which might have been expected from the equilibrium data. For example, in run 3 which was operated at a column top temperature of 120°C, the average composition of the distillate collected was approximately 8% propylene glycol by mass.

It is felt that if this work were to be carried out on the plant, the continuous heating system used would mean that large and sudden variations in the column top temperature would be less likely to occur than in the laboratory where the heat was thermostatically controlled and switched on and off as required. The results achieved on the plant should, therefore, be more stable and glycol losses may be slightly higher.

5.3.5 The Effect of an Increased Column Top Temperature in the Absence of a Nitrogen Purge

The experimental batches produced at a higher column top temperature had shown that it was difficult to accurately control the head temperature. However, earlier work on nitrogen purging had already shown that more stable operating conditions could be achieved without a continuous purge. Eliminating the purge during the distillation process was also proving to be successful on the production scale. It was decided, therefore to carry out two further experiments to establish whether the improved stability of the operating conditions would improve the results obtained at 110°C and 120°C. The experiments were not repeated at higher temperatures because the results had already indicated that there was little benefit to be gained from operating at a column top temperature in excess of 120°C. The results from these further runs are summarised in Table 5.4.

Table 5.4 Effect of Column Top Temperature on Reaction Time and Glycol Loss Without Nitrogen Purge

Run No	Column Top Temp (°C)	Reaction Time (hrs)	Glycol Lost (g)	Glycol Lost (% of charge)
6	110	7.0	5.65	1.0
7	120	6.5	11.36	2.0

5.3.6 Effect of Nitrogen Purge at Higher Column Top Temperatures - Discussion of Results

The results in Table 5.4 suggest that the effect of eliminating the nitrogen purge has been the reverse of what might have been expected. Both runs show a slight increase in reaction time and a significant increase in the quantity of glycol lost from the reactor. However, the overall picture is more complex. During the experiment it was noticed that the runs without a nitrogen purge show much less fluctuation in the column top temperature than those where nitrogen was continuously applied. The stable operating conditions meant that the majority of the distillate collected was recovered at or about the correct temperature. This was not always possible in the presence of a constant inert gas flow because dramatic changes in the head temperature meant that the distillate was refluxed to the reactor and subsequently recovered at a lower temperature.

5.3.7 Conclusions

(i) The reaction time for the first stage of the resin manufacture decreases with an increase in column top temperature up to a temperature of 120^{o}C.

(ii) Above 120^{o}C the reaction rate is independent of column top temperature.

(iii) An increase in column top temperature results in an increase in the loss of propylene glycol from the reactor.

(iv) The column top temperature becomes more difficult to control at higher temperatures.

(v) The follow up experiments carried out in runs 6 and 7 confirm earlier work that the column top temperature can be more easily controlled in the absence of a constant inert gas flow.

5.4 Assessment of the Performance of Existing Separation Equipment

The method for the estimation of the vapour flowrate in the Reactor 6 overheads described in section 5.2.3, was based on the assumption that equilibrium was reached within the system. It was decided that checks should be carried out to establish whether or not equilibrium was being achieved in the overhead systems for both Reactor 6 and Reactor 7. The simplest way to check this was to take samples of the top product at various times throughout a batch of resin. The sample can then be analysed for propylene glycol content. The composition of the sample can be compared with the theoretical composition of a equilibrium mixture obtained at the recorded column top temperature. Some samples of liquid returned to the reactor were also collected so that some idea of the degree of separation achieved within the column could be obtained. A few typical results are tabulated in table 5.5.

Table 5.5 Review of Top Product Vapour Composition and Column Top Temperature

Batch	Recorded Top Temp (°C)	Actual Composition % P/G (w/w)	Theoretical Composition % P/G (w/w)	Theoretical Top Tem (°C)
Reactor 6				
Resin A/568	105 103	6.5 10.25	1.5 0.5	114.5 123.5
Resin E/153	104 109	13.0 17.0	1.0 3.0	124.0 128.5
Resin B/251	102 105	15.5 13.0	0.5 1.5	127.0 124.0
Reactor 7				
Resin A/569	102 112	37.0 39.25	0.5 5.0	147.0 149.0
Resin B/250	102	33.0	0.5	147.0

The variations shown above were typical of all the samples collected. However, there was one major difference between Reactors 6 and 7. It was found that the composition of the samples collected from the top of the partial condenser on Reactor 6 varied with variations in vapour temperature although there was always a greater than expected glycol content. Samples collected from the top of the fractionating column on Reactor 7 always had a composition of 30-40% propylene glycol by mass. The vapour composition appeared to be independent of the reaction conditions.

These findings could be explained by three factors:

(i) Inaccurate measurement of column top temperature.

(ii) High glycol content of top product achieved by physical carryover of liquid in the vapour stream caused by high vapour velocities.

(iii) Equilibrium is not being reached within the overhead system.

5.4.1 Column Top Temperature Indication on the Production Plant

The temperature indicators situated at the top of Reactors 6 and 7 are listed instruments for the purposes of BS5750 and are calibrated at regular intervals. The siting of the probes was therefore considered. The Reactor 6 column top temperature probe is situated directly above the partial condenser and must, therefore, be in the vapour stream. This is verified by the fact that the composition of the top product does vary in line with variation in recorded column top temperature.

Examination of the Reactor 7 packed column showed that the temperature probe is situated opposite, and slightly above the vapour duct to the condenser. It is recommended that this probe is re-sited into the mouth of the vapour duct to ensure that it is directly in the vapour stream.

5.4.2 Determination of Vapour Velocities in the Reactor Overhead Equipment

In order for the high glycol content of the top product to be caused by physical carryover a vapour velocity of several meters per second is necessary. Using the vapour flowrates for Reactors 6 and 7 from section 3 velocities of 0.43 m/s and 0.9 m/s respectively have been calculated. See Appendix D for calculations.

5.4.3 Calculation of the Minimum Wetting Rate for the Packed Column on Reactor 7

While calculating the vapour flowrates for Reactor 7 it was noticed that the reflux rate of 0.04 m^3/hr was extremely low for a packed column of 0.56 m diameter. It was felt that this could explain why vapour liquid equilibrium was not being achieved. It was decided that this rate should be checked against a calculated minimum wetting rate for the packing in the column which is thought to be 3.75 cm ceramic saddles. From Perry(14)the minimum effective liquid rate is or 0.4m^3/hr m^2. This is calculated by dividing the volumetric flowrate per unit area by the surface area of the packing per unit volume (194 m^2/m^3).

Superficial liquid rate for Reactor 7 $= \frac{0.04}{0.24} = 0.17$ m^3/hr m^2

$$\text{Irrigation rate} = \frac{0.17}{194} = 8.76 \times 10^{-4}\ \text{m}^2/\text{hr}$$

This means that for Reactor 7 to reach even the minimum liquid flow rate it is necessary to increase the liquid reflux by a factor of 440. This would mean a rate of 17.6 m^3/hr water returned to the column top. This is obviously impractical since the addition of this quantity of water would prevent the reaction proceeding. It is therefore, impossible to get adequate separation of water and propylene glycol from the Reactor 7 packed column whilst the distillate reflux process is in use.

5.5 Conclusions

The work reported in this chapter provides an important basis for the design work to be carried out initially on the prototype overhead system to be installed on Reactor 5 and on the final Reactor 7 design. In particular, it has highlighted the tendency to design equipment which is too large for the intended application and indicated some of the problems which can arise from this practise. It is intended that following the implementation of an experimental system on Reactor 5 it will be possible to design a partial condenser system for Reactor 7 which can operate efficiently over a range of conditions.

CHAPTER 6

THE DESIGN, INSTALLATION AND OPERATION OF OVERHEAD EQUIPMENT ON REACTOR 5

CHAPTER 6

THE DESIGN, INSTALLATION AND OPERATION OF OVERHEAD EQUIPMENT ON REACTOR 5

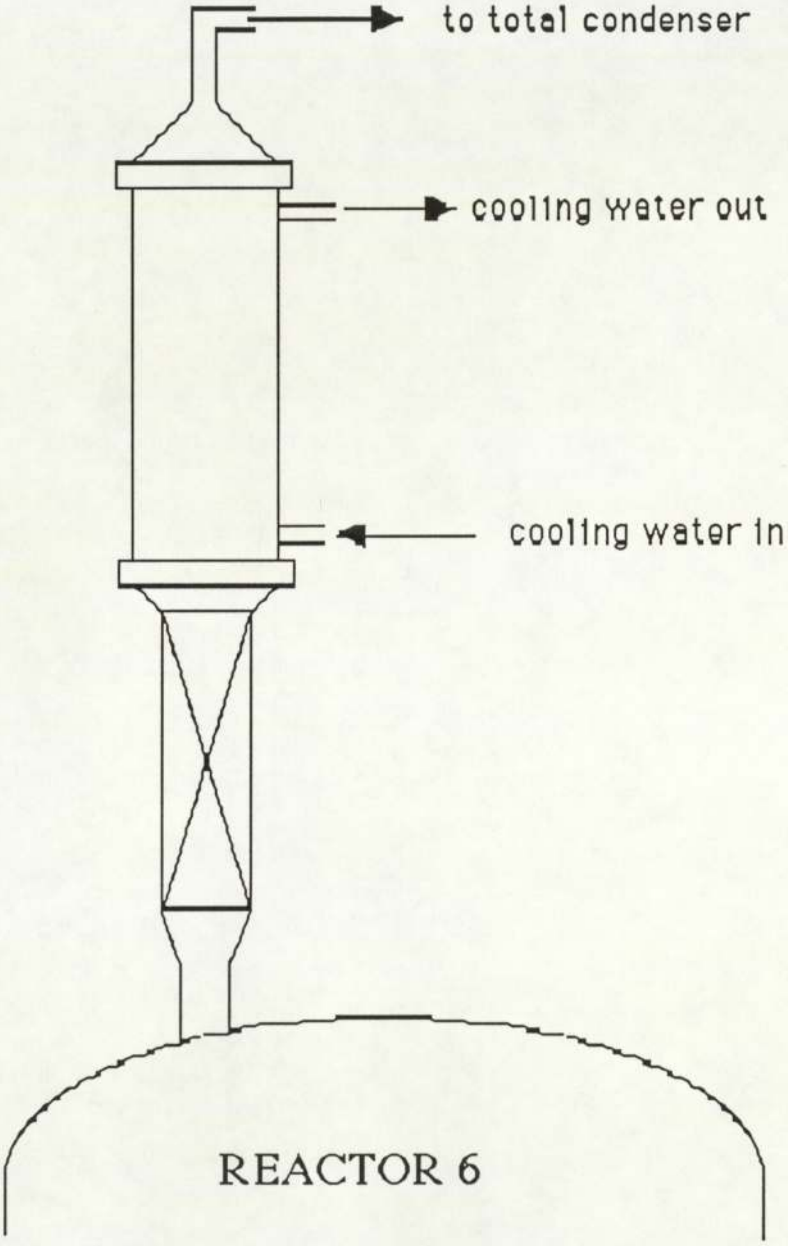
6.1 Introduction

The work discussed in the previous chapter provided information on vapour and liquid flowrates which could be used in the design of new equipment. In addition, consideration of the orientation of existing overhead equipment had indicated several areas for improvement. From this information it was possible to develop a 'prototype' system for installation on a small polyester reactor, Reactor 5. This equipment could then be used to investigate further the glycol water separation process and help to produce a final design proposal for the larger Reactor 7. This chapter discusses the development and installation of the partial condenser equipment on Reactor 5. The operation and performance of the new equipment is then discussed.

6.2 Orientation of Overhead Equipment for Reactor 5

A redundant shell and tube heat exchanger was available on site which could be mounted on Reactor 5 as part of a prototype for the new design on Reactor 7. It was initially intended that the Reactor 5 system should be based on the set up already in use on Reactor 6. However, the calculation of the fluid flowrates in the Reactor 7 packed column had indicated that the column diameter was too large. It was decided therefore to give some consideration to the orientation and sizing of the equipment on Reactor 6. Vapour and liquid flowrates estimated from Reactor 6 were used to check the physical sizing of the available equipment proposed for the Reactor 5 system. This was particularly important because the available heat exchanger was smaller than that installed on Reactor 6. It was therefore necessary to ensure that the heat exchanger was large enough to provide sufficient heat transfer and flow areas to cope with the worst case situation during resin manufacture. These calculations are detailed in Appendix E.

Figure 6.1 Layout of reactor overhead equipment



After ensuring that the equipment was not undersize for the intended application, it was then necessary to consider how it was to be installed and what information was required from the prototype rig. After considering the orientation of the equipment on Reactor 6 it was realised that the equipment was not arranged for optimum performance. From the diagram shown in figure 6.1 it can be seen that the equipment consists of a vertical partial condenser sited directly above a short packed column. The liquid flow to the top of the packed column is not fed through a distributor because it is assumed that the vertical tubes will effectively distribute the liquid across the packing cross-section. However, the heat exchanger has a wider diameter than the column, so if it is assumed that each tube in the heat exchanger condenses the same mass of vapour during operation, it is found that in excess of fifty percent of the liquid leaving the condenser flows directly down the packed column wall and hence takes no part in the mass transfer operation. In order to prevent this situation occurring on Reactor 5, the packed section selected had the same internal diameter as the heat exchanger.

A further problem on the Reactor 6 system had been observed in the early days of its operation. A report by Hounsell(16) stated that reaction times on Reactor 6 were extended and analysis of samples from the packed section showed that approximately 75 % of the liquid returning to the reactor was water. Confirmatory work carried out as part of the current project has shown that this is, in fact, conservative and results well in excess of eighty per cent water by mass were obtained. These findings indicate that the partial condenser on Reactor 6 is oversize and that consequently a large proportion of the water vapour is being condensed along with the propylene glycol vapour. However, a closer examination of figure 6.1 indicates another problem. It can be seen that the cooling water on the shell-side of the partial condenser operates co-currently, that is, it enters at the bottom of the heat exchanger and leaves at the top. This is an effective way of operating a vertical exchanger because it ensures that the shell is full at all times. However, in this case the coolant is water fed directly from the plant cooling tower at about 25°C. The temperature of the vapour entering the bottom of the partial condenser is unknown but it will clearly be in excess of 100°C. Therefore at the entrance to the partial condenser the vapour will meet a tube wall with a temperature difference in the order of 75°C. This very large temperature 'shock' may result in the condensation of water as well as glycol at the bottom of the partial condenser. This is particularly likely to be true when there is low vapour flow, and hence low velocity such as towards the end of the reaction.

Early work carried out on the Reactor 6 overhead equipment, and work carried out on partial condenser systems by raw material suppliers(15) suggested that the majority of the mass transfer took place within the partial condenser. However, Kern(12) indicates that partial condensers are extremely ineffective as mass transfer stages and should not be relied upon. It was decided therefore, that the performance of the heat exchanger and of the packed section should be determined from the system on Reactor 5 so that the final design for Reactor 7 would be as effective as possible. Consequently, the equipment was installed with sample points at the top and bottom of the packed section to enable liquid samples to be taken for analysis. Also, to determine the effectiveness of the vertical heat exchanger, resistance thermometers were installed at various positions within the exchanger to determine the radial and vertical temperature profiles within the exchanger during resin manufacture. The resistance thermometers were linked to a chart recorder so that any changes which occurred during the process could be monitored. In order to do this it was necessary to assume that temperature could be used as an indication of composition within the partial condenser, ie no superheat existed. This was felt to be a reasonable assumption within the heat exchanger because any superheat in the vapour as it left the reactor was likely to have been lost before the vapour left the packed section.

6.3 Commissioning of Reactor 5 Overhead System

Once installed it was decided that the partial condenser system on Reactor 5, similar in layout to figure 6.1, should be commissioned by carrying out a reactor boil with a mixture of propylene glycol and water. This would enable the system to be leak tested, the resistance thermometers to be checked and would enable the condensing performance of the partial condenser itself to be tested. In order to save on raw material costs it was decided that the distillate from Reactor 7 should be collected to provide the propylene glycol and water mixture. Approximately two tonnes of distillate was collected and when analysed was found to have a glycol content of approximately 30% by mass. This would correspond to a boiling point of 108^{o}C. It was decided that an additional 450 litres of propylene glycol should be added to increase the boiling point of the mixture and to increase the enthalpy change across the partial condenser to enable the temperature profile to be established. It was estimated that the increased glycol content (to approximately 45% by mass) would raise the boiling point of the mixture to 115^{o}C.

The first stage of the commissioning run involved carrying out a 'dry-run' with the instrument engineers to ensure that the correct valves opened and closed for each of the overhead modes selected. The fail safe operation of the overhead system was also checked. The chart recorder for the resistance thermometers sited in the partial condenser and the vapour duct was then checked. It was found that one of the resistance thermometers had been broken during installation and it was not possible to obtain a reading from that channel. All other channels appeared to be working correctly.

The boil up of the distillate mixture was taken very slowly at first in order to ensure that the partial condenser system was not overloaded. The water flow rate to the partial condenser was initially set at 900 lph in line with established practice on Reactor 6. After approximately fifteen minutes the cooling water inlet to the partial condenser shell began to leak and it was necessary to stop heating the reactor to enable the leak to be repaired. Following repair, the cooling water rate was again set to 900 lph and the heat was reapplied to the reactor. At a reactor temperature of 85°C, vapour was seen to be escaping from the joint between the top of the partial condenser and the vapour duct. Significant quantities of vapour were not expected at such low temperatures. Once the source of the leak had been located the reactor was again cooled back to enable the necessary repairs to be made. Fifteen minutes after reheating, the reactor temperature recorder was reading 85°C but liquid could be seen returning from the bottom of the total condenser to the separator. The partial condenser top temperature was reading 94°C at this stage and it was assumed that boiling was occurring at the reactor wall but that the body of the liquid was not heated to boiling temperature. The temperatures being recorded by the resistance thermometers were then checked against the partial condenser top temperature reading in the plant. It was found that most of the recorded temperatures were of the same range as the plant reading, but that one of the channels (the temperature of the vapour leaving the partial condenser) was reading approximately twenty degrees lower than the rest.

Shortly after the start of the distillation, samples were taken from the effluent line and from the sample points at the top and bottom of the packed section in line between the reactor and the partial condenser. The partial condenser top temperature recorder on the plant was reading 94°C, and the sample was found to have a propylene glycol content of approximately 15% by mass, extremely high for that temperature. However, the sample had been taken downstream of the separator and it was assumed that the high glycol content was due to mixing of the distillate with effluent from the previous batch of resin produced on the reactor. The analysis of the samples of liquid return taken from the packed section showed that the composition of the liquid stream did not change over the packed height of the column. The two samples taken from the top and bottom of the packed section were found to have a glycol composition of approximately five per cent by mass. This corresponds to an equilibrium temperature of 101°C in the packed column. The temperature recorded in the bottom third of the partial condenser at this time was 98°C. Whilst a temperature difference of 3°C seemed reasonable between the bottom of the partial condenser and the top of the packed section, it was a matter of concern that all temperatures appeared to be lower than expected. For example, at a partial condenser top temperature of 94°C it would be expected that all vapour generated is condensed in the partial condenser and that there is no condensation in the total condenser. However, this was not found to be the case.

It is of some concern that the samples collected from the packed section beneath the partial condenser had the same composition, hence indicating that no mass transfer is taking place in the partial condenser. If this is found to be the case, the efficiency of the overhead system would obviously be affected. Shortly after the distillate samples were taken, the packing in the section immediately beneath the partial condenser began to rattle and it was noticed that the pressure in the reactor had increased to over 75 mbars. By this time the reactor temperature had increased to 90°C and the column top temperature was reading 98°C. The heat to the main reactor was immediately switched off and the pressure was released through the main fractionating column. As a result of this the high temperature alarm on the condensate return at the bottom of the total condenser was sounded and it was necessary to allow the reactor to cool until the condensate temperature had returned to normal. The heat to the reactor was slowly reapplied and again the pressure in the reactor began to increase. Once more the pressure was released through the fractionating column and the heat to the reactor was shut off. On the third attempt, the pressure again began to rise in the reactor and the run was abandoned.

At no time during the commissioning boil out did any of the temperatures recorded in the overhead system exceed 100°C. This suggested, therefore, that the partial condenser was not thermally overloaded at any time. It was noted however, that the duct which feeds the vapour from the reactor to the partial condenser is of a much smaller cross-sectional area than the partial condenser itself and it may be possible that this duct has insufficient cross-sectional area to allow the vapour to leave the reactor quickly enough.

Several problems were encountered when the reactor was handed back to resin manufacture which may explain some of the events noted during the commissioning boil. Firstly, a batch of resin made shortly after the reactor was handed back was found to be slightly coloured. It is possible that this may be as a result of contamination from a batch of a special resin made some weeks earlier. Although the reactor had been boiled out with a caustic solution and again with water after the completion of the specialist resin, the partial condenser system had not been fully installed and had not been used. It is known that some of the resin boiled up into the bottom of the fractionating column during processing because blockages were experienced at the time. It is possible, therefore, that some resin was also deposited in the line to the partial condenser which had not been cleared during the caustic boil.

An alternative explanation for the unexpected results obtained during the commissioning boil is that the reactor temperature probe may have been faulty. It has already been stated that at all times during the boil out the reactor temperature was reading a lower temperature than that recorded in the partial condenser. At the time this was thought to be because boiling was taking place at the reactor wall without the body of the reactor contents reaching the boiling temperature. However, several days later the reactor temperature probe suffered complete failure and had to be replaced. It seems likely, therefore, that the temperature of the reactor contents was much higher than that recorded resulting in a higher rate of boil up. The rate of condensation in the partial condenser then resulted in a very high rate of liquid return, and the packed section beneath the partial condenser flooding resulting in an increased pressure in the reactor. However, this was not thought likely to cause problems during resin manufacture when the vapour load would be significantly lower.

In conclusion, the commissioning run highlighted several areas for potential problems when the partial condenser system is used for the manufacture of polyester resins. The objectives of the boil out had been to check that the equipment and the instrumentation worked in the correct manner; to determine initial control conditions of the partial condenser as a guide for the manufacture of the first polyesters using that system; and to determine a temperature profile across the partial condenser. This profile could then be used as a guide to the performance of the partial condenser and the flow patterns of the vapour within it. Of the three objectives, only the first was achieved, with some limited success. However, it was felt that enough was learned about the system to allow a polyester to be safely produced on Reactor 5 by the fusion process.

6.4 Resin Manufacture Using the Partial Condenser System on Reactor 5

Following the commissioning of the overhead equipment, the trials on Reactor 5 were continued with the manufacture of a batch of resin H. Resin H is an orthophthalic based polyester which is normally produced by the solvent process. However, the requirements of one particular customer made it preferable to make some batches by the fusion process. This made it an ideal resin for the first batch using the new equipment since it would be possible to transfer back to the solvent process in the event of problems with the partial condenser. The manufacture of this batch proceeded without difficulty although the process time was found to be two to three hours longer than the average. This was not felt to be significant in view of the known inconsistency of reaction times on the plant. The final properties of the resin were found to be slightly out of balance at the bottom of both the acid value and the viscosity specifications. This may be due to an increased glycol content in the resin following decreased losses during processing when compared with the Reactor 6 system. However, it would be necessary to produce further batches to establish whether this were the case.

Throughout the reaction stage of this batch, samples of the liquid return were taken from the top and bottom of the packed section to determine the degree of separation within the packing. On average, the liquid returning to the reactor had a composition of 70% propylene glycol by mass and the liquid at the top of the packing had a composition of approximately 5% propylene glycol by mass. The effluent from the total condenser had a glycol composition of 15% in the early stages of the reaction but this quickly dropped to a consistent level of 5% by mass. These results are the opposite of those obtained during the commissioning boil out. In that case the indication was that no mass transfer was taking place within the packed section. During resin production, the analysis of the samples shows that virtually all the mass transfer takes place within the packed section and that the partial condenser can be ignored as a mass transfer stage.

Following the successful production of the batch of resin H with the new partial condenser, a series of fusion process resins were made on Reactor 5. Once sufficient batches had been produced, a review of the process times was carried out. It was found that process times were consistently much greater on Reactor 5 than those on Reactor 6. It was felt that the reason for these greatly extended reaction times was due to a delay in switching from the partial condenser system to the by-pass, possibly as a result of incorrect temperature measurement at the top of the partial condenser. The partial condenser coped well with the increased vapour load early on in the reaction and this enabled the reaction top temperature to be quickly achieved without losing control of the partial condenser top temperature. Because of this, it was felt that, with further work, the performance of the Reactor 5 system could be significantly improved.

It was recommended that a mass flowmeter should be installed on the effluent line. This could then be used by the operator to indicate when the bulk of the water of reaction had been removed. Since the chosen meter worked by measuring the density of the liquid passing through, it would also be possible to use this to indicate when excess glycol was being lost to the effluent line. The operator could then use this information as a guide to determine when to switch from the partial condenser to the by-pass condenser. This work has since been carried out along with a detailed analysis of batch process times and this has been reported elsewhere(17).

6.5 Conclusions

(i) Resins can be successfully produced by the fusion process on the Reactor 5 partial condenser system.

(ii) Early results from resin production indicate that virtually all the mass transfer takes place in the packed section. This is contrary to the results obtained during the glycol/water boil.

(iii) Extended process times were encountered on the Reactor 5 system which are believed to be due to delays in switching from the partial to the bypass condenser.

(iv) The experimental work indicated that temperature measurement can cause some problems on this process and highlights the need for reliable, well maintained instruments.

(v) The use of a mass flowmeter is recommended to determine when the changeover should take place.

CHAPTER 7

THE DESIGN OF THE REACTOR 7 PARTIAL CONDENSER

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THE DESIGN OF THE REACTOR 7 PARTIAL CONDENSER

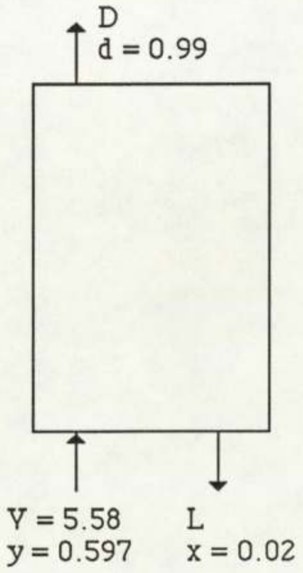
7.1 Introduction

This chapter describes the work involved in generating the final design of the partial condenser of Reactor 7 and the operation of the system once installed. Two design strategies were considered and investigated. The first strategy assumed that all mass transfer occurred in the partial condenser, and that the packed section exists purely to ensure that the vapour entering the heat exchanger is well mixed and that all subliming acids are washed back into the reactor. In the second strategy it is assumed that the mass transfer takes place in the packed section which acts as the enriching section of a distillation column. The partial condenser condenses just enough water to generate sufficient reflux to wet the packing.

7.2 Strategy 1 Design of the Partial Condenser System

7.2.1 The Mass Balance

Figure 7.1



BASIS: 1 HOUR

Compositions expressed in terms of mole fractions of water

Assumptions:

(i) The flowrate and composition of V is based on previous work on Reactor 6.

(ii) The composition of D is specified as 0.99 mole% H_20.

(iii) The composition of L is found from equilibrium data.

Overall Balance:

$$V = D + L \qquad - \qquad 7.1$$

Balance on water:

$$Vy = Dd + Lx \qquad - \qquad 7.2$$

substituting,

$$Vy = (V-L)d + Lx$$

and,

$$L = \frac{V(y-d)}{(x-d)} = 5.58\,\frac{(0.597 - 0.99)}{(0.02 - 0.99)}$$

$$L = 2.26 \text{ kmols}$$

Hence, from equation 7.1

$$D = 3.32 \text{ kmols.}$$

7.2.2 Determination of Heat Load

The condenser was split into 5 zones to enable the heat load to be calculated. Previous calculations had shown that the quantity of heat to be removed desuperheating the vapour to the dew point was negligible compared with the quantity of heat to be removed during the condensation. Therefore, the desuperheating section has been ignored in this calculation.

The temperature ranges selected for each zone are as follows:

Zone 1	163 - 159°C
Zone 2	159 - 152°C
Zone 3	152 - 134°C
Zone 4	134 - 114°C
Zone 5	114 - 105°C

For each zone, the V/L ratio was determined by the trial and error method described by Kern(12). In order to simplify the illustration, only the successful iterations have been included. In summary, the equilibrium constants for each component can be found for a specific temperature from the vapour and partial pressures if the properties of an ideal gas are assumed using equation 7.3 below:

$$K_i^T = \frac{P_i^T}{P_t} \qquad - \qquad 7.3$$

where,

K_i^T = equilibrium constant of component i at temperature T

P_i^T = vapour pressure of component i at temperature T

P_t = total pressure of the system

Zone 1: Vapour Feed = 5.58 kmols.

Propylene glycol	= 2.25 kmols	= 0.403 mole fraction
Water	= 3.33 kmols	= 0.597 mole fraction
		1.000

$K_{pg}^{159} = 0.379$.

$K_w^{159} = 6.113$

assume $\frac{V}{L} = 7.5$

Liquid condensed across zone 1

Propylene Glycol = 0.586 kmols
Water = 0.071 kmols
Total = 0.657 kmols

Zone 2: Vapour Feed

Propylene Glycol = 1.664 kmols = 0.338 mole fraction
Water = 3.259 kmols = 0.662 mole fraction
4.923 kmols 1.000

$K_{pg}^{152} = 0.291$

$K_{w}^{152} = 4.962$

assume $\frac{V}{L} = 5.6$

Liquid condensed across zone 2

Propylene Glycol = 0.633 kmols
Water = 0.113 kmols
Total = 0.776 kmols

Zone 3: Vapour Feed

Propylene Glycol = 1.031 kmols = 0.247 mole fraction
Water = 3.146 kmols = 0.753 mole fraction
Total = 4.177 kmols 1.000

$K_{pg}^{134} = 0.144$

$K_{w}^{134} = 3.007$

assume, $\frac{V}{L} = 3.1$

Liquid condensed across zone 3

Propylene Glycol = 0.712 kmols
Water = 0.304 kmols
Total = 1.016 kmols

Zone 4: Vapour Feed

Propylene Glycol = 0.319 kmols = 0.101 mole fraction
Water = 2.842 kmols = 0.899 mole fraction
Total = 3.161 kmols 1.000

$K_{pg}^{114} = 0.062$

$K_{w}^{114} = 1.616$

assume $\frac{V}{L} = 3.87$

Liquid condensed across zone 4

Propylene Glycol = 0.257 kmols
Water = 0.392 kmols
Total = 0.649 kmols

Zone 5: Vapour Feed

Propylene Glycol = 0.062 kmols = 0.025 mole fraction
Water = 2.450 kmols = 0.975 mole fraction
Total = 2.512 kmols 1.000

$K_{pg}^{105} = 0.040$

$K_{w}^{105} = 1.193$

assume $\frac{V}{L} = 8$

Liquid condensed across zone 5

Propylene Glycol = 0.047 kmols
Water = 0.232 kmols
Total = 0.279 kmols

Composition of Vapour leaving the system

Propylene Glycol = 0.015 kmols = 0.007 mole fraction
Water = 2.218 kmols = 0.993 mole fraction
Total = 2.233 kmols 1.000

Total Liquid returned to the Reactor

Propylene Glycol= 0.586 + 0.633 + 0.712 + 0.257 + 0.047 = 2.235 kmols

Water = 0.071 + 0.113 + 0.304 + 0.392 + 0.232=1.112 kmols

NB: The enthalpy of propylene glycol liquid is calculated from equation 7.4:

$$C_p = \left(\frac{\delta H}{\delta T}\right)_P \qquad - 7.4$$

where,

H = enthalpy, kJ/kg
C_p = specific heat capacity, kJ/kg^{o}C
T = temperature, ^{o}C
P = pressure, = 760 mm Hg

The datum temperature is taken as 0 ^{o}C

Table 7.1 Determination of Enthalpies of Vapour and Liquid Streams

Temp	Propylene Glycol Vapour (kg)	Enthalpy kJ/kg	H_2O Vapour (kg)	Enthalpy (kJ/kg)	H_{vap} (MJ)	Propylene Glycol Liquid (kg)	Enthalpy kJ/kg	Water Liquid (kg)	Enthalpy (kJ/kg)	H_{liq} (MJ)	Total Enthalpy (MJ)
163	171	1290	60	2762	386.3						386.3
159	126.5	1279	58.7	2757	323.6	44.5	523	1.3	670	24.1	347.7
152	78.4	1258	56.6	2749	254.2	48.1	493	2.0	640	25.0	279.2
134	24.2	1198	51.2	2731	169.1	54.1	413	5.5	582	25.5	194.6
114	4.7	1148	44.1	2697	124.3	19.5	348	7.1	478	10.2	134.5
105	1.1	1124	39.9	2683	108.3	3.6	313	4.2	440	3.0	

Table 7.2 Total Heat Content of Streams Leaving the Zones

T_{vap} (°C)	Enthalpy of combined streams (MJ)	Change in enthalpy $q = \Delta H$ (MJ)	Δtw (°C)	tw (°C)	Δtav (°C)	$q/\Delta tav$ (MJ/°C)	q_{cum} (MJ)
163	366.3	38.6	2.1	35.0	127.1	0.304	0
159	347.7	68.5	3.7	32.9	124.5	0.550	38.6
152	279.2	84.6	4.6	29.2	179.8	0.471	107.1
134	194.6	60.1	3.3	24.6	101.1	0.594	191.7
114	134.5	23.2	1.3	21.3	88.9	0.261	251.8
105	111.3			20.0			275.0

Table 7.3 Summary of Overall Heat Load of Partial Condenser

T_{vap}°C	H (MJ)	$q=\Delta H$ (MJ)	Δt_w (°C)	t_w (°C)	ΔT_{av}(°C)	$q/\Delta t$	q_{cum}
163	386.3	38.6	2.1	35	127.1	0.304	0
159	347.7	68.5	3.7	32.9	124.5	0.550	38.6
152	279.2	84.6	4.6	29.2	179.8	0.471	107.1
134	194.6	60.1	3.3	24.6	101.1	0.594	191.7
114	134.5	23.2	1.3	21.3	88.9	0.261	251.8
105	113.3		20				275.0

where,

H = total enthalpy of the streams at that temperature (MJ)
t_w = cooling water temperature (°C)
Δt_w = Difference in water temperature across zone (°C)
Δt_v = vapour temperature (°C)

$$\Delta t_{av} = \frac{(t_{v1} - t_{w2}) + (t_{v2} - t_{w1})}{2} \qquad - \qquad 7.5$$

Water Side Calculations

assume, $t_{in} = 20^oC$

$t_{out} = 35^oC$

$\Delta t_w = 15^oC$

C_p = specific heat capacity of water = 4.1868 kJ/kg^{o}C

M = mass flowrate of water, kg/hr

Total Heat Load = Q = q_{cum} = 275 MJ

and,

$$Q = MC_p\Delta t_w \qquad - \qquad 7.6$$

Hence the mass flowrate of cooling water can be determined:

$$M = \frac{275 \times 10^3}{4.1868 \times 15} = 4379 \text{ kg/hr}$$

Finally, the weighted temperature difference across the condenser can be calculated.

$$\Delta T_{av} = \frac{\Sigma q}{\Sigma UA} = \frac{275}{2.180}$$

$$\Delta T_{av} = 126^oC$$

7.2.3 Specification of the Heat Exchanger

It is assumed that the heat exchanger consists of 61 tubes constructed of 16 swg stainless steel. The tubes have an outside diameter of 1.9 cm and are arranged on a 2.5 cm triangular pitch. The tubes are 1 m in length with baffles spaced 15 cm apart.

The heat exchanger will be mounted vertically with the process fluids on the tube side and the cooling water in the shell.

7.2.4 Shell-side Heat Transfer Coefficient

From table 7.3,

$M = 4379$ kg/hr
$Q = 275$ MJ
$\Delta T_{av} = 126\ ^{o}C$ = weighted temperature difference

Shell-side coefficient

A_S = Heat transfer surface area for subcooling on water side, m^2

$$A_S = \frac{ID \times C'B}{P_t} \qquad - \qquad 7.7$$

ID = internal diameter of shell = 0.254 m
C' = clearance between tubes = 0.0064 m
B = baffle spacing = 0.15 m
P_t = tube pitch = 0.025 m

$A_S = 9.8 \times 10^{-3}\ m^2$

G_S = mass velocity of cooling water, kg/hr m^2
t_a = average shell-side temperature = 27.5 ^{o}C
μ = 0.86 cp = 3.1 kg/m hr
j_H = Factor for Heat Transfer, based on the physical properties of the cooling water at its average temperature (27.5^{o}C), and the shell side Reynolds Number, Re_S, correlation from Kern(12).

$$j_H = \frac{h_o D_e}{k} \times \left(\frac{C_p \mu}{k}\right)^{-1/3} \times \left(\frac{\mu}{\mu_w}\right)^{-0.14} \qquad - \qquad 7.8$$

where,

h_o = heat transfer coefficient for outside fluid, kJ/hr m^2 ^oC

D_e = equivalent diameter for heat transfer and pressure drop

= 0.019 m

k = thermal conductivity, = 2.23 kJ/hr m ^oC

C_p = specific heat capacity, = 4.40 kJ/hr m^2 ^oC

μ_w = viscosity at wall temperature, assume unchanged.

= 3.1 kg/m hr]

$$Re_s = \frac{D_e G_s}{\mu} = 2716$$

From correlation, $j_H = 26$

hence,

h_o = 5584 kJ/hr m^2 ^oC

7.2.5 Tube-side Heat Transfer Coefficient

From table 7.4,

$Q = 375 \times 10^3$ kJ

T_V = average vapour temp = 134 ^oC

It is possible to calculate the tube wall temperature by estimating the internal heat transfer coefficient, h_{io}, using equation 7.9:

$$t_w = t_a + \left[\frac{h_{io}}{h_{io} + h_o}\right](T_v - t_a) \qquad - \qquad 7.9$$

Assume h_{io} = 2900 kJ/hr m^2 ^oC

Hence, t_w = 63.9 ^oC. Assume the liquid film on the inside of the tubes has the properties of propylene glycol at 64 ^oC.

μ_f = 26 kg/m hr

k_f = 0.732 kJ/hr m ^oC

ρ_f = 1012 kg/m^3

g = gravitational constant due to acceleration, = 127 x 10^3 m/hr^2.

L_c = condensate loading for vertical tubes, kg/hr m

$$L_c = \frac{L}{\Pi N_t D} \qquad - \qquad 7.10$$

L = total mass flowrate of condensate,

= (1.112 x 18) + (2.235 x 76) = 190 kg/hr

N_t = number of tubes in heat exchanger, = 61

D = internal diameter of tubes, = 0.016 m

L_c = 62 kg/hr m

The tube side Reynolds Number, Re_t, can now be calculated:

$$Re_t = \frac{4L_c}{\mu_f} = 9.5$$

The average value of the condensing film heat transfer coefficient can be estimated from the Reynolds Number using the correlation of Colburn(18). However, the minimum Reynolds Number used in this correlation is 100, hence it is necessary to extrapolate from the available data for the very low Reynolds Number obtained in this design to generate equation 7.11.

$$h_{av} \left(\frac{\mu_f^2}{k_f^3 \rho_f^2 g} \right)^{1/3} = 0.81 \qquad - \qquad 7.11$$

h_{av} = h_i = 3423 kJ/hr m^2 ^oC

This value can now be adjusted for wall thickness by multiplying by the ratio of the internal to external diameters:

$$h_{io} = \frac{0.0016}{0.0019} \times 3423 = 2882 \text{ kJ/hr m}^2 \,{}^{o}\text{C}$$

This compares well with the assumed value of 2900 kJ/hr m^2 ^{o}C.

The Clean Overall Heat Transfer Coefficient can now be calculated.

$$U_C = \frac{h_{io} h_o}{h_{io} + h_o} \qquad - \qquad 7.12$$

U_C = 1505 kJ/hr m^2 ^{o}C.

Using a dirt coefficient, R_d, of 0.001 an adjusted heat transfer coefficient can be calculated.

$$U_D = \frac{U_C}{1+R_d U_C} \qquad - \qquad 7.13$$

U_D = 600 kJ/hr m^2 ^{o}C

The actual required tube length, L_t, can now be calculated.

$$A = \frac{Q}{U_D \, \Delta T_{av}} = 3.6 \text{ m}^2$$

and,

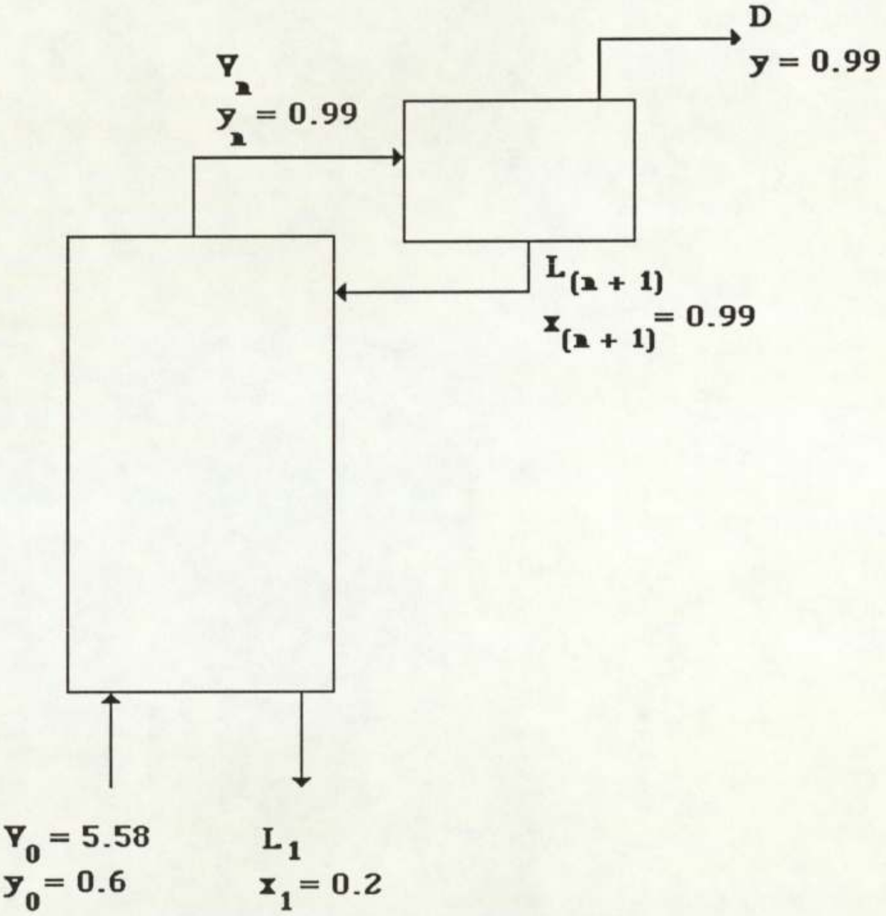
$$L_t = \frac{A}{\Pi \, D \, N_t} = 1.2 \text{ m}$$

7.3 Strategy 2 The Packed Column and Partial Condenser System

7.3.1 The Mass Balance

Figure 7.2 Packed Column System Schematic of Process Flows

The flowrates are expressed in terms of Molar flow on a one hour time basis. Mole fractions are expressed as fraction of water (the most volatile component.



A reflux ratio of 1 is considered an economic minimum.

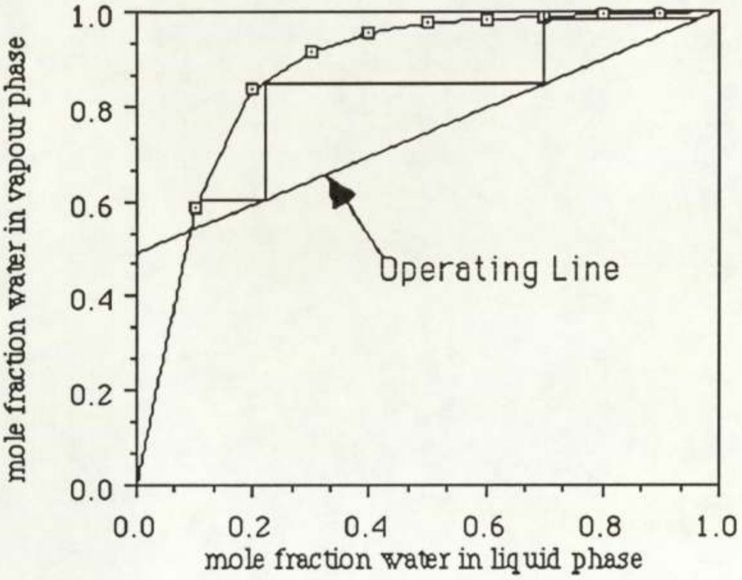
Hence, $D = L_{n+1}$

It is assumed that no mass transfer takes place in the partial condenser.

Hence, $y_n = x_{n+1} = y_d =$ specified at 0.99.

x_1 is in equilibrium with the vapour leaving the first stage. From the equilibrium diagram, shown in figure 7.3, $x_1 = 0.20$.

Figure 7.3 Vapour Liquid Equilibrium Diagram (22)



Overall Balance:

$V_o = D + L_1$

$D = 5.58 - L_1$ - 7.14

Overall Balance over most volatile component (mvc)

$V_o y_o = D y_d + L_1 x_1$ - 7.15

substituting from equation 7.14:

$L_1 = 2.75$ kmols

Hence, $D = 2.83$ kmols

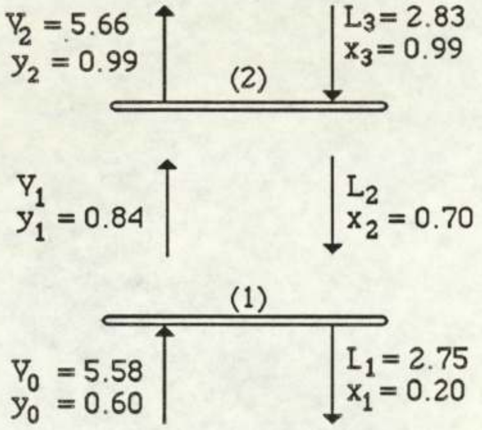
Molar Balance over Partial Condenser

$$V_n = D + L_{n+1}$$

However, a reflux ratio of 1 has been selected. Therefore,
$D = L_{n+1} = 2.83$ kmols

Hence,
$V_n = 5.66$ kmols

Figure 7.4 Stagewise Molar Balance



Balance over Stage 1 (refer to Figure 7.4)

Overall:-
$V_o + L_2 = V_1 + L_1$
$V_1 = 2.83 + L_2$ - 7.16

Balance of mvc over Stage 1

$V_o y_o + L_2 x_2 = V_1 y_1 + L_1 x_1$

$0.70 L_2 = 0.84 V_1 - 2.80.$ - 7.17

substitute for V_1 from equation 7.16:
$L_2 = 3.00$

and,

$V_1 = 5.83.$

Check for balance over Stage 2:

$V_1 y_1 + L_3 x_3 = V_2 y_2 + L_2 x_2$

$7.70 = 7.70$

7.3.2 Summary of Mass Flowrates, basis one hour

V_0 Molar Rate = 5.58 kmols/hr = 506.8 lb/hr

Mole Fn		*Total Mass*	*Mass Fn*
0.4	Propylene Glycol	169.6	0.74
0.6	Water	60.3	0.26
		229.9	

V_1 Molar Rate = 5.83 kmols/hr = 350.5 lb/hr

Mole Fn		*Total Mass*	*Mass Fn*
0.16	Propylene Glycol	70.9	0.45
0.84	Water	88.2	0.55
		159.1	

V_2 Molar Rate = 5.66 kmols/hr = 231.9 lb/hr

Mole Fn		*Total Mass*	*Mass Fn*
0.01	Propylene Glycol	4.3	0.04
0.99	Water	100.9	0.96
		105.2	

L_1 Molar Rate = 2.75 kmols/hr = 390.4 lb/hr

Mole Fn		*Total Mass*	*Mass Fn*
0.80	Propylene Glycol	167.2	0.94
0.20	Water	9.9	0.06
		177.1	

L_2 Molar Rate = 3.0 kmols/hr = 234.1 lb/hr

Mole Fn		*Total Mass*	*Mass Fn*
0.30	Propylene Glycol	68.4	0.64
0.70	Water	37.8	0.36
		106.2	

L_3 Molar Rate = 2.83 kmols/hr = 116.0 lb/hr

Mole Fn		*Total Mass*	*Mass Fn*
0.01	Propylene Glycol	2.2	0.04
0.99	Water	50.4	0.96
		52.6	

7.3.3 The Packed Column Design

The packed column must be designed to ensure that the superficial liquid flowrate is sufficient to wet all of the packing and hence ensure efficient mass transfer. However, it is also important that the cross-sectional area is large enough to ensure a reasonable pressure drop across the column height and avoid flooding.

This column has been designed using a method described by Treybal(19). The correlations used in this book are given in imperial units. Consequently it has been necessary to design the column in imperial units and convert the final results to SI. The cross-sectional area has been specified such that the maximum flowrate of vapour leaving the column corresponds to 60% of the flow required to flood the column.

The flood point is determined from the correlation by Eckert(20), shown in equation 7.14:

$$\frac{L'}{V'}\left(\frac{\rho'_v}{\rho'_L}\right)^{1/2} = K_1\frac{(V')^2 C_f(\mu'_L)^{0.2}}{g'_c\rho'_v\rho'_L} \times \left(\frac{\rho'_w}{\rho'_L}\right) \quad - \quad 7.14$$

From the mass balance it can be seen that the maximum flowrates of liquid and vapour occur at the bottom of the packed column. Both of these streams have a high concentration of propylene glycol. They are assumed, therefore, to have the physical properties of propylene glycol at 150 ^{o}C, the temperature at which the streams are in equilibrium.

L' = superficial liquid mass flowrate, lb/hr ft^2.
V' = superficial vapour mass flowrate, lb/hr ft^2.
K_1 = empirical constant obtained from graphical correlation$^{(20)}$,
g'_c = gravitational constant due to acceleration
= 4.18×10^8 lb mass/lb force hr^2
$\rho_{L'}$ = density of liquid, lb/ft^3
$\rho_{V'}$ = density of vapour, lb/ft^3
μ'_L = viscosity of liquid, cpoise

The column is assumed to be packed with 5/8" metal Pall rings.
C_f = packing factor = 70.
A_c = cross-sectional area of packed section, ft^2.
$\rho_{L'}$ = 60.81 lb /ft^3.
$\rho_{V'}$ = 0.14 lb/ft^3.
$\rho_{W'}$ = density of water
= 62.43 lb/ft^3.
μ'_L = 1 cp.

From the mass balance, the mass flowrates are:

L_1 = 390.4 lb/hr $\qquad$ V_0 = 506.8 lb/hr

$$L' = \frac{L_1}{A_c}\ \text{lb/hr ft}^2 \qquad V' = \frac{V_0}{A_c}\ \text{lb/hr ft}^2$$

hence,

$$\frac{L'}{V'}\left(\frac{\rho'_V}{\rho'_L}\right)^{1/2} = 0.037$$

From the graphical correlation this corresponds to a value of K_1 equal to 0.18. Therefore, from equation 7.14,

$$V'_{flood} = 2985 \text{ lb/hr ft}^2$$

Hence, at 60% flood

$$V' = 1791 \text{ lb /hr ft}^2.$$

However, later on in the reaction the composition of the vapour will change. Hence, to ensure that the column can cope with all circumstances, the above calculation will be repeated assuming that the vapour has the density of steam at 150 °C.

In this case, $K_1 = 0.20$ and, $V'_{flood} = 1764.2 \text{ lb/hr ft}^2$.

At 60 % flood, $V' = 1058.5 \text{ lb /hr ft}^2$.

Hence the column must be designed for the second case and the dimensions of the column can now be determined.

$$A_c = \frac{V_0}{V'} = 0.479 \text{ ft}^2 \left(= 0.04 \text{ m}^2\right)$$

and the internal diameter of the column, d = 9.4 in(= 0.23m).

The packed column is therefore designed to have an internal diameter of 10 inches and a cross-sectional area of 0.545 ft^2. The superficial flowrates can now be determined:

$V' = 930 \text{ lb/hr ft}^2$; $L' = 716 \text{ lb/hr ft}^2$

The mass transfer coefficients will be calculated at the bottom, the centre and the top of the packed column, as these correspond to the equilibrium stages, and the compositions and flowrates have been determined from the mass balance.

The mass transfer coefficients are dependent on the available surface area and on the degree of holdup in the column. The holdup is expressed in terms of the operating holdup ϕ_o and the static holdup, ϕ_s. The operating holdup consists of the column of liquid which is constantly moving through the column. The static holdup is that which is retained in the column after the liquid and vapour flows have stopped and the column is allowed to drain. The liquid which is held up statically quickly reaches equilibrium with the vapour and contributes little to the mass transfer.

The liquid holdup is expressed as ft^3 liquid /ft^3 packed volume.

The surface area of the packing is expressed in terms of the diameter of a sphere which has the same surface area as one particle of packing. The correlation data obtained from Treybal(19) is only available for 1/2" diameter ceramic Raschig rings. However, the relative contact area of this packing is similar to that of 5/8" metal pall rings and hence the results achieved from this calculation should be directly comparable.

The interfacial areas and holdups are first calculated for liquid water. In this case the subscript w is used.

The holdup calculations are based on the diameter of a sphere which has the same surface area as a single particle of packing, d_s.

For 1/2" Raschig rings:

d_s = 0.0582 ft
A_a = specific interfacial surface for distillation, ft^2 /ft^3 packed volume
H = correction factor
ϕ_t = total holdup = $\phi_o + \phi_s$.

7.3.4 The Bottom of the Column

Flowrates:

L and V are the superficial molar flowrates of the liquid and vapour, respectively.

From the mass balance:

L'_m = 11.12 lb moles /hr ft^2

L' = 715.8 lb /hr ft^2

V'_m = 22.55 lb moles /hr ft^2

V' = 929.2 lb /hr ft^2.

Physical Properties of propylene glycol at 150°C:

μ'_L = viscosity = 1 c poise

ρ'_L = density = 60.81 lb /ft^3

σ' = surface tension = 33 dynes /cm

μ''_v = viscosity (lb /ft hr) = 0.027 lb /ft hr (assumed to be the same as propyl alcohol)

ρ'_v = 0.14 lb /ft^3

From the work of Shulman(21):

$$A_{aw} = m(V')^n(L')^p \qquad - \qquad 7.15$$

where,

A_{aw} = average specific interfacial surface for mass transfer, based on an air-water system ft^2/ft^3.

For 0.5 inch Raschig rings and 500 < L' < 1500, the coefficients are as follows:-

m = 8,200

n = $(3.15 \times 10^{-4})L' - 0.30$ = - 0.075

p = - 1.04

However, the vapour is assumed to have a density of 0.075 lb /ft^3 for the purposes of this correlation. In order to adjust for the correct density (V'_{mod}) must be determined as follows and replaced for V' in equation 7.15:

$$V'_{mod} = V'\left[\frac{0.075}{\rho_v}\right]^{0.5} = 680.1 \text{ lb/hr ft}^2$$ - 7.16

Hence,
A_{aw} = 5.40 ft^2/ft^3 packed volume.

For holdup calculations refer to correlation equations by Shulman(21).

$$\phi_{tw} = \frac{2.25 \times 10^{-5} L'^{\beta}}{d_s^2}$$ - 7.17

where, $b = 0.965 d_s^{0.376}$ - 7.18

$b = 0.331$

Hence, $\o_{tw} = 0.0585.$

$$\phi_{sw} = \frac{0.00104}{d_s^{1.21}}$$ - 7.19

$\o_{sw} = 0.0325$

Hence,

$\o_{ow} = 0.0585 - 0.0325$

$\o_{ow} = 0.026.$

$$\phi_s = \frac{6.85 \times 10^{-5} \mu'^{0.02}_L \sigma'^{0.99}}{d_s^{1.21} \rho'^{0.37}_L}$$ - 7.20

$\o_s = 0.0149$

$$H = \frac{0.897 L'^{0.57} \mu'^{0.13}}{\rho'^{0.84}_L \left(0.1183 L'^{0.43} - 1\right)} \left(\frac{\sigma'}{73}\right)^{(0.925 - 0.262 \log L')}$$ - 7.21

$H = 1.051$

$\o_o = \o_{ow} H$ - 7.22

$\o_o = 0.0273$ ft^3 liquid /ft^3 packed volume.

$$A_a = A_{aw} \frac{\phi_o}{\phi_{ow}} \qquad - \qquad 7.23$$

A_a = 5.67 ft^2 /ft^3 packed volume.

ϕ_t = 0.0422 ft^3 liquid /ft^3 packed volume.

e = fractional void in a dry packed bed.

= 0.84 ft^3 /ft^3 packed bed for 5/8" pall rings.

e_o = operational void fraction in an irrigated bed, ft^3 /ft packed bed.

$$e_o = e - \phi_t \qquad - \qquad 7.24$$

e_o = 0.7978 ft^3 /ft^3 packed volume.

The mass transfer co-efficient can now be calculated using equation 7.25 by Shulman:

$$\frac{k'_v Sc_v^{2/3}}{V'_m} = 1.195 \left(\frac{d_s V'}{\mu''_v (1-e_o)} \right)^{-0.36} \qquad - \qquad 7.25$$

where,

k'_v = vapour-phase mass transfer coefficient, lb moles /hr ft^2.

Sc_v = vapour-phase Schmidt number

$$Sc_v = \frac{\mu''_v}{\rho'_v D_v} \qquad - \qquad 7.26$$

μ''_v = 0.027 lb/ft hr

ρ'_v = 0.14 lb /ft^3

D_v = 0.45 ft^2/hr

Sc_v = 0.43

hence,

k'_v = 1.747 lb moles /hr ft^2 = k'_y

Liquid Phase Coefficient.

Physical Properties of Liquid

D_L = 6.01×10^{-5} ft^2 /hr

μ'_L = 1 c poise

μ''_L = 2.419 lb /ft hr

ρ'_L = 60.81 lb /ft^3

Sc_L = 662

$$\frac{d_s k_L}{D_L} = 25.1\left(\frac{d_s L'}{\mu''_L}\right)^{0.45} Sc_L^{0.5} \qquad - \qquad 7.27$$

k_L = 2.401 lb moles /hr ft^2 (lb moles /ft^3).

ρ'_{Lm} = molar density = 0.80 lb moles /ft^3.

k'_x = liquid phase mass transfer coefficient

k'_x = $k_L \times \rho'_{Lm}$ = 1.921 lb moles /hr ft^2 mol fn.

7.3.5 Mass Transfer Coefficients at the Middle and the Top of the Packed Column

The above calculations have been repeated for the conditions at the centre and the middle of the packed column. The values of the properties used are detailed in Appendix F. In summary, the equilibrium temperature at the middle of the column is 112°C. The properties of the vapour and liquid streams are assumed to be average properties of water and propylene glycol at this temperature.

The equilibrium temperature at the top of the column is 105°C. The vapour and liquid streams are assumed to have the properties of steam and water respectively at 105°C.

The mass transfer coefficients obtained are summarised below:

Centre: $k'_y = 1.478$ lb moles/hr ft^2; $k'_x = 4.665$ lb moles/hr ft^2

Top: $k'_y = 1.367$ lb moles/hr ft^2; $k'_x = 10.626$ lb moles/hr ft^2

7.3.6 Summary of Packed Column Values

Table 7.4

	x	0.20	0.70	0.99
V'm	$\frac{\text{lb moles}}{\text{hr ft}^2}$	22.55	23.57	22.88
A_a	ft^2/ft^3	5.67	7.20	18.354
k'y	$\frac{\text{lb moles}}{\text{hr ft}^2}$	1.747	1.478	1.367
k'x	$\frac{\text{lb moles}}{\text{hr ft}^2}$	1.921	4.665	10.626
	$-\left[\frac{k'x}{k'y}\right]$	- 1.100	- 3.156	- 7.77

Table 7.5 Further Calculated Values for the Packed Column

y	y_i	A_a	V'm	k'_y	(V'm)y	$\frac{1}{k'_y A_a (y_i - y)}$
0.60	0.68	5.67	22.55	1.747	13.53	1.262
0.65	0.88	6.00	22.76	1.669	14.79	0.434
0.70	0.94	6.31	22.97	1.635	16.08	0.404
0.75	0.968	6.62	23.18	1.578	17.39	0.439
0.80	0.98	6.95	23.40	1.522	18.72	0.525
0.84	0.984	7.20	23.57	1.478	19.80	0.653
0.90	0.992	11.80	23.41	1.433	21.07	0.643
0.95	0.999	16.40	23.18	1.395	22.02	0.892
0.99	1.00	18.35	22.88	1.367	22.65	3.987

The value of y_i is obtained by drawing a line of slope $(-k'_x/k'_y)$ from the operating line to the equilibrium line as shown in figure 7.5. The intersection of this line with the equilibrium line gives the value of y_i. By drawing a vertical line from y_i to y in each case and then linking these points, it is possible to obtain a reference line allowing y_i to be determined for each value of y.

Interim values of V'_m, A_a and k'_y are obtained from graphs of the calculated data against y. These are shown in figures 7.6 - 7.8.

The height of packing required, Z, can be found from equation 7.28:

$$Z = \int_{V'_m y_0}^{V'_m y_2} \frac{d(V'_m y)}{k'_y A_a (y_i - y)} \qquad - \qquad 7.28$$

The value of Z is found by the graphical integration of the above equation, see figure 7.9. The area under the graph is found to be equivalent to 6.54 ft height of packing, and this is rounded up to give a design height of 7 ft, or 2.15m.

Figure 7.5 Reference Diagram for the Determination of y_i

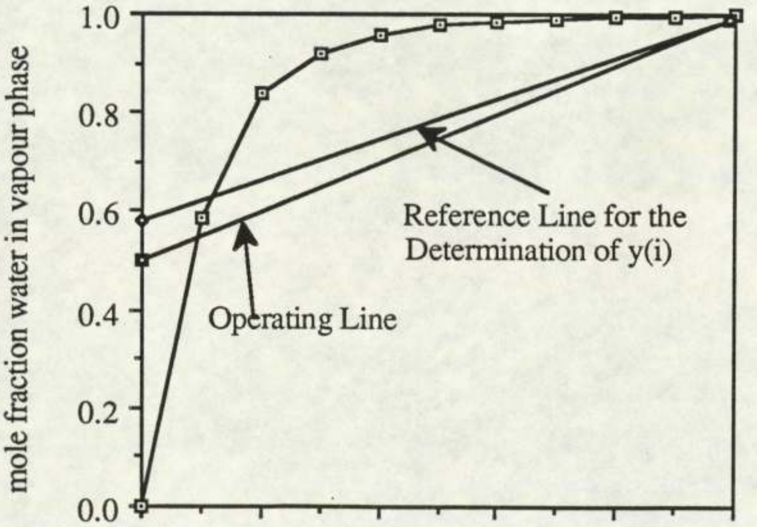


Figure 7.6

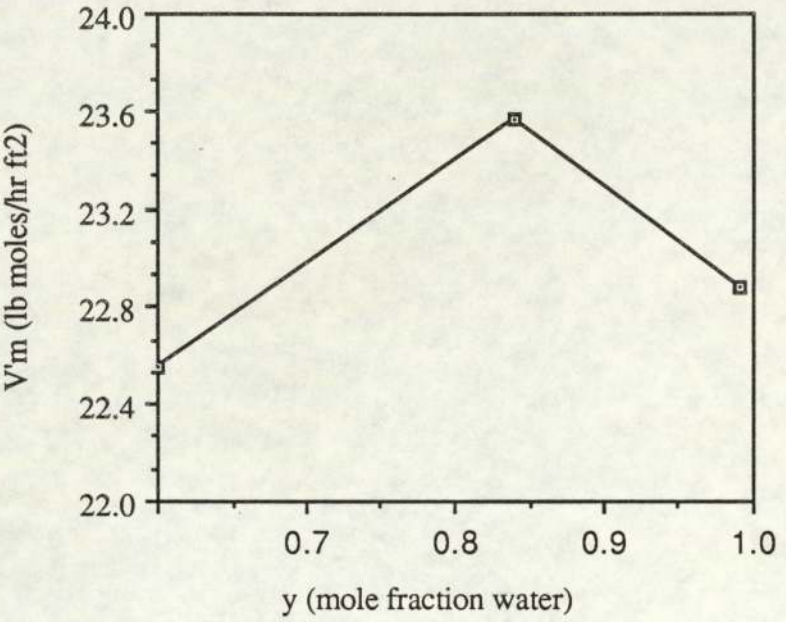

Correlation of Superficial Molar Flowrate Against Vapour Composition

Figure 7.7

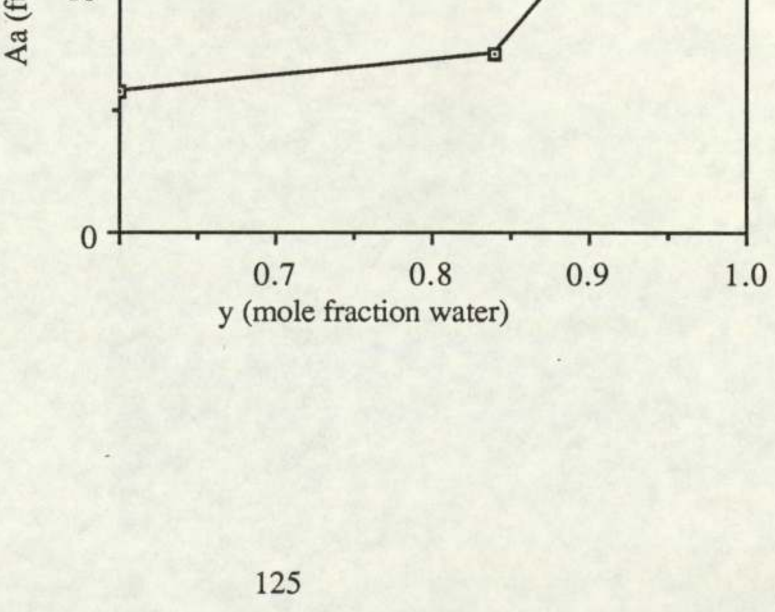

Correlation of Superficial Surface Area Against Vapour Composition

Figure 7.8

Correlation of Vapour Mass Transfer Coefficient Against Vapour Composition

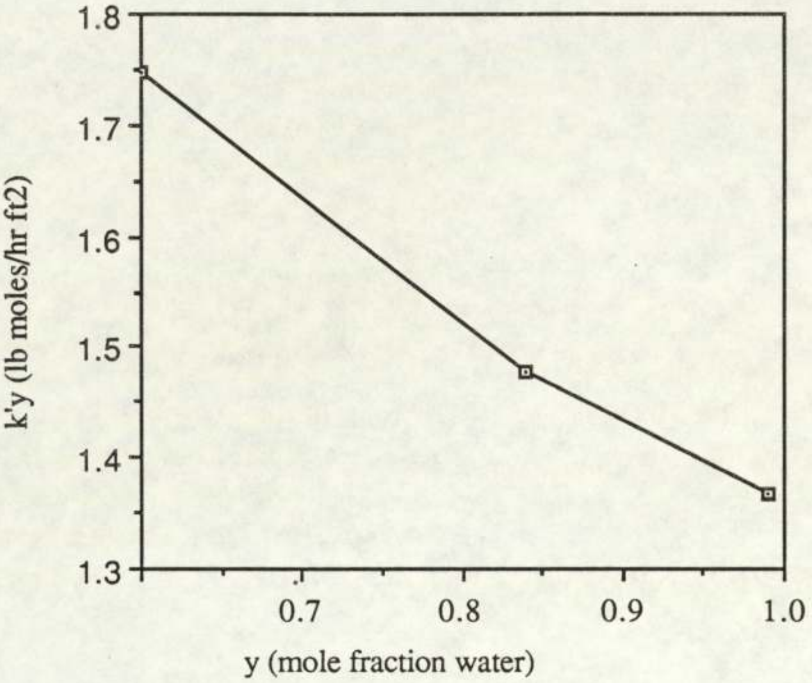
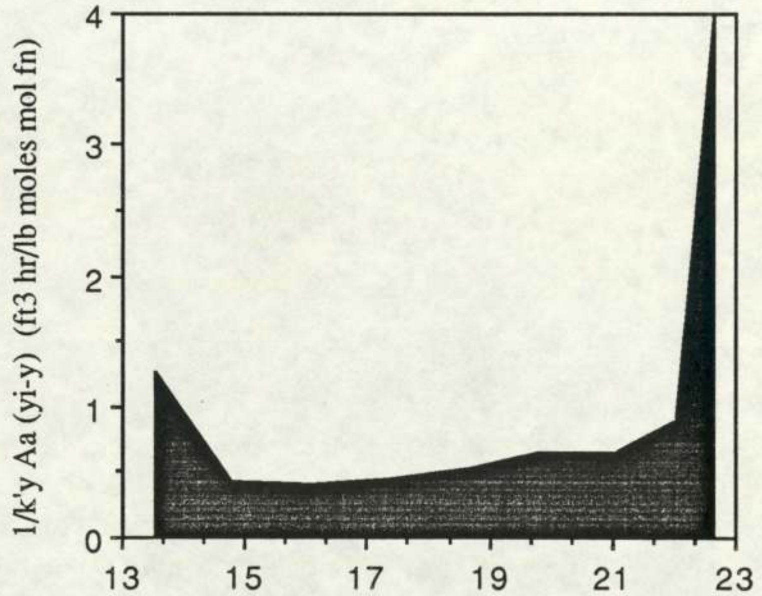


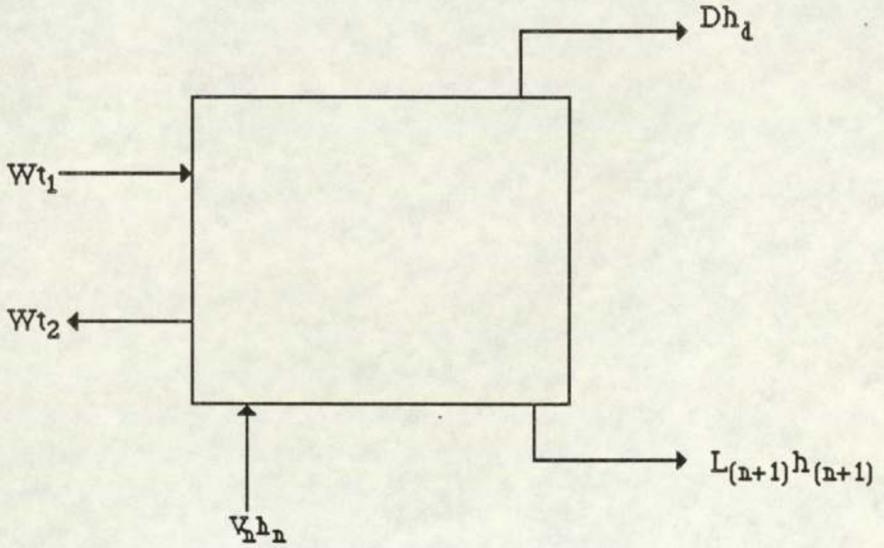
Figure 7.9

Graphical Integration to Determine the Packed Height Required



7.4 Packed Column System - Partial Condenser Design

Figure 7.10 Partial Condenser Design -Heat Balance



Heat Balance:

$V_n h_n \; - \; L_{n+1} h_{n+1} \; - \; Dh_d \quad = \quad WCp\,(t_2 \; - t_t).$

where, V^n, L_{n+1}, D are molar flowrates kmoles /hr :

h_n, h_{n+1}, h_d are enthalpies of streams, kJ /kmol.

Cp = specific heat capacity of water = 4.1868 kJ /kg°C.

W = mass flowrate of cooling water, kg /hr.

t_1, t_2 = temperature of cooling water entering and leaving the partial condenser, respectively, °C.

It is assumed that no mass transfer takes place in the partial condenser. Therefore from section 7.3.1:

V_n = 5.66 kmols/hr. $\quad y_n$ = 0.99.

L_{n+1} = 2.83 kmols/hr. $\quad y_{n+1}$ = 0.99.

D = 2.83 kmols/hr. $\quad y_{n+1}$ = 0.99.

All streams are assumed to have the properties of water or steam at 105°C and that no sensible heat is removed.

Therefore,

h_n = h_d = 48,348 kJ/kmol.
h_{n+1} = 8028 kJ/kmol.

Hence, total heat to be removed:

5.66 * 48,348 - 2.83 * 48,348 - 2.83 * 8,028 = 114,106 kJ.

Assume a cooling water temperature rise (t_2 - t_1) of 10°C.

114,106 = W * 4.1868 (10).
W = 2725 kg /hr.

Calculate flowrates at bottom of partial condenser.

Vapour flowrate = 5.66 kmols /hr.
= 105.16 kg /hr.
= 231.84 lb /hr.

Liquid return = 2.83 kmols /hr.
= 52.58 kg /hr.
= 115.92 lb.hr.

Vapour flowrate at top of partial condenser = 52.58 kg /hr.
Assume density of vapour = 0.7003 kg /m^3.

Hence,
volumetric flowrate, Q = 75.08 m^3 /hr.

Viscosity of vapour = 0.0122 cp
= 0.044 kg /m hr.

Assume 3/4"outside diameter tubes = 0.016 m.

To ensure the condenser performs efficiently, it is necessary that the vapour flow at the top of the condenser is turbulent. Hence, calculate for Reynolds number of 5000.

$$Re_t = \frac{Dv\rho}{\mu}$$

where v = vapour velocity, m/hr

therefore,

v = 19 634 m/hr

A = cross-sectional area

A = Q/v = $3.82 * 10^{-3}$ m^2.

The total number of condenser tubes can be calculated from equation 7.29:

$$N_t = \frac{4A}{\Pi D^2} = 19 \qquad - \qquad 7.29$$

This was felt to be too small once the condenser started to scale. Therefore, the dimensions for a practical condenser were selected as; 36 tubes, 0.016 m external diameter on 0.024 m triangular pitch, 16 swg stainless steel, 0.2 m internal shell diameter. However, it is important to establish that the condenser will still operate under turbulent conditions at the minimum flowrate at the top of the condenser.

Total area available for flow = 7.24×10^{-3} m^2

hence vapour velocity, v = 10 270 m/hr

Re = 2640.

Hence, turbulent flow is still likely at the top of the partial condenser.

It is proposed that the partial condenser is situated vertically above the packed column. Condensation takes place on the tube side at a constant temperature of 105°C. The vapour and condensate are assumed to have the properties of steam and water respectively. The condenser operates under countercurrent flow and a cooling water temperature difference of 10°C is assumed, ie cooling water enters at the top of the partial condenser at 20°C and leaves at the bottom at 30°C.

The design of the partial condenser is carried out by the same method as that described for the 'partial condenser system' in Section 7.2. The calculations are given in Appendix G. The condenser is found to have a tube length of 0.46 m. There are no baffles on the shell side.

7.5 The Selection and Installation of the Overhead System for Reactor 7

After due consideration of the two systems, the combined packed column and partial condenser system was selected for use on Reactor 7. This was chosen for two reasons. Firstly, there were indications in the literature(12) that partial condensers were unreliable as the sole source of mass transfer, particularly once they had been in operation for some time. Secondly, samples taken from the packed section on Reactor 5 indicated that a significant amount of mass transfer took place under normal operating conditions. It was also felt that the operation of the partial condenser as a constant temperature reflux condenser would be very stable. Once selected, the equipment was estimated to have an installed cost of £28 000. This would have a payback time of approximately 4 months based on the rate of glycol loss alone. It was felt that the partial condenser system would also have a beneficial effect on the process times, but this was impossible to quantify. The expenditure for the project was approved and the system was installed and became operational in June 1990.

7.6 Conclusions

After several months operation of the new partial condenser system, the average cost benefits for a batch of Resin B, which is normally produced on Reactor 7, were found to be as follows:

(i) Improved Reaction Times

On average, process times were found to be reduced from 39.5 hours to 32 hours, an improvement of 16%.

(ii) Reduced Raw Materials Losses

The need for in-process glycol additions has been removed by the operation of the partial condenser. This is equivalent to an average saving of 250 kg of propylene glycol per batch.

(iii) Increased Yield

The rate of loss of glycol from the reactor has been reduced to such a level that the standard glycol excess added to the formulation can be reduced. However, instead of taking this action, the overall charge to the reactor has been increased hence increasing the yield. On average, an additional 1.2 tonnes per batch can be obtained.

Production figures from 1989 and 1990 indicate that an average of one hundred batches of Resin B per annum are produced on Reactor 7. Therefore, assuming the increased plant availability is used to produce more resin B, and allowing for raw material savings, cost benefits of approximately £158 000 per annum can be achieved. However, Resin B is used as a base resin for the production of gel coat resins where spare capacity is available. Consequently, the real benefits of the partial condenser could be substantially greater.

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LIST OF APPENDICES

APPENDIX A

Cost Analysis of Cryogenic Nitrogen vs Pressure Swing Adsorption Nitrogen

The annual rate of usage of cryogenic nitrogen on the polyester plant is expected to be 352 280 m^3, taking into account the reduction in usage following the adoption of the modified purging programme. The Pressure Swing Adsorber is charged according to the hours of operation. Although other production units also use nitrogen produced by the PSA system, the polyester plant is by far the most significant user and the other operations will be ignored for the purposes of this illustration. It is assumed that the unit is operated for a total of 2800 hours per annum.

The total annual cost of nitrogen using the new purging programme is calculated below:

Cryogenic Nitrogen Charges

	£
Annual service charge/rental	8888
240 000 m^3 @ £7.06 per 100m^3	16966
112 280 m^3 @ £5.56 per 100m^3	6243
	32097

PSA nitrogen system annual costs

	£
Annual service charge	4000
2800 hrs @ 52p/hr	1456
Electricity 305 kW for 2800 hrs	3160
@ £0.037 per kWhr	8616

Total overall cost = £40 713

Estimated Future Nitrogen Costs Using Solely PSA Nitrogen

The total annual requirement of nitrogen is 570 680 m^3. The current PSA unit produces nitrogen at a range of 78 m^3/hr. Consequently, it would be necessary to operate the system for a total of 7316 hours per annum. This would mean operating the PSA system for 22.5 hours per day for 330 days each year. Such a loading is unlikely to give an acceptable level of cover for breakdown and routine maintenance. Therefore it has been assumed that an additional unit would be required. Assuming the conditions of lease for a new system are the same as for the existing pressure swing adsorber, the annual costs would be as follows:

Annual Nitrogen Costs if PSA Nitrogen is used exclusively

	£
Annual service/rental charge 2 x 4000	8000
7316 hours @ 52p/hr	3804
Electricity 30.5 kW for 7316 hrs @ £0.037 per kWhr	8256
Total	**20060**

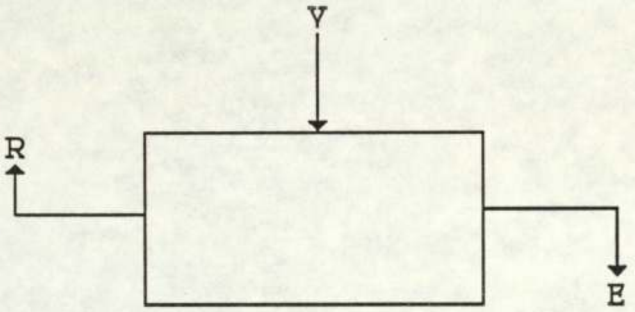
This corresponds to an annual saving of £20653. Assuming the installation costs for the second PSA unit to be £12 000, a payback time of seven months would be achieved.

APPENDIX B

Calculation of Vapour Loadings on Reactor 7 Packed Column Based on Rate of Collection of Distillate

It is possible to estimate the rate of vapour flow through the packed column if the level in the buffer tank is assumed to be constant over a specified time span. The buffer tank is situated in the effluent line from the condenser to provide a small reservoir of distillate which can be used as reflux to the packed column. A mass balance can therefore be carried out over the tank as shown in figure B.1:

Figure B.1 Mass balance over Reactor 7 Buffer Tank (assuming constant level).



V = condensed vapour kg/hr
E = effluent kg/hr
R = reflux kg/hr

The mass balance was carried out during the manufacture of a number of batches of polyester. The maximum flowrate was obtained during the production of a batch of Resin B when 220 kg of distillate were collected in 50 minutes. The reflux rate was 36 litres/hr. The collected distillate was well mixed and then sampled. It was found to have a density of 1.0287 kg/dm^3, corresponding to a propylene glycol content of 41 % by mass.

Therefore over unit time V = R+E. From the data obtained:

$$E = 220 \times \frac{60}{50} = 264 \text{ kg/hr}$$

Assuming the reflux and effluent streams have the same composition:

$$R = 36 \times 1.0287 = 37 \text{ kg/hr}$$

Therefore, $V = 264 + 36 = 300$ kg/hr

APPENDIX C

Estimated Mass Balance Over The Reactor 6 Overhead Equipment

In the first stage of Resin A the charge is as follows:

32.29 kmols Diol

9.82 kmols Di-Carboxylic Acid

One mole of glycol reacts with one mole of acid to give one mole of polyester and one mole of water.

For the batch in question,the first distillate was collected when the reaction temperature was 171^{o}C. Assuming that at this temperature the first water is generated and has not yet left the reaction mixture, the solution contains x kmoles of water.

Reaction mixture composition:

Diol	32.29 - x kmoles
Dicarboxylic Acid	9.82 - x kmoles
Water	x kmoles
Polyester	x kmoles
Total	42.11

At the reactor temperature the components have the following vapour pressures:

Propylene glycol = 440 mm Hg

Water = 6101 mm Hg

The Dicarboxylic acid and the resin are assumed to be involatile at this temperature.

The partial pressure of each component is related to its concentration in the liquid phase. Assume the reaction mixture is at atmospheric pressure and,

$$P = x_1 p_1 + x_2 p_2 \qquad \text{C.1}$$

$$p_a = x_a P_a \qquad \text{C.2}$$

where,

P = total pressure

x_a = mole fraction of component a in the liquid phase

p_a = vapour pressure of component a at stated temperature

P_a = partial pressure of component a

Substituting the available data into equation C.1:

$$760 = \left[\frac{(32.29 - x)}{42.11} \times 440 \right] + \left[\frac{x}{42.11} \times 6101 \right]$$

Hence,

$x = 3.14$ kmoles

From Raoults Law:

$$P_a = P y_a \qquad \text{C.3}$$

where y_a = molar fraction of component a in the vapour phase

Hence,

$$760 = \left[\frac{(32.29 - x)}{42.11} \times 440 \right] + \left[\frac{x}{42.11} \times 6101 \right]$$

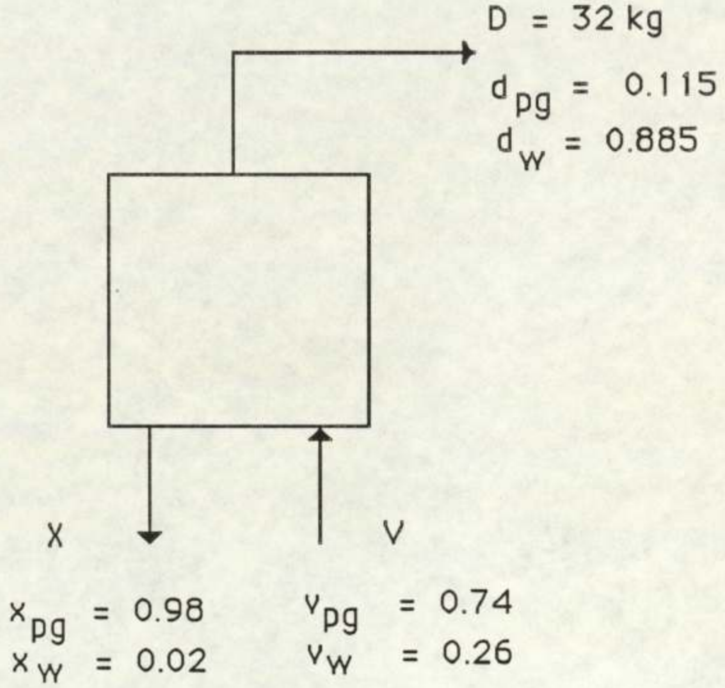
$$y_w = \frac{6101 \times 3.14}{42.11 \times 760} = 0.60$$

It is preferable to work in terms of mass fractions, in which case, the compositions are:

$$y_{pg} = 0.74$$
$$y_w = 0.26$$

The top product collected during a second batch of Resin A was generated at an average rate of 32 kg/hr and had an initial composition of 11.5 % by mass propylene glycol. The composition of the initial liquid return was not available but if it is assumed to be in equilibrium with the vapour stream it will have a mass fraction of 0.98 propylene glycol. See the vapour-liquid equilibrium graph, figure 7.3.

Figure C.1 Mass Balance Over Reactor 6 Overhead system (basis 1 hr)



Total balance: V = 32 + X C.4

Water balance:

0.26V = 32(0.885) + 0.02X C.5

Substitution gives:

X = 83.33 kg/hr
V = 115.33 kg/hr

APPENDIX D

VAPOUR VELOCITIES IN REACTOR 6 AND 7 OVERHEAD SYSTEMS

Reactor 6

From Appendix C a vapour flowrate of 115 kg/hr was calculated for reactor 6. This distillate had a composition of 40% molar propylene glycol and 60% molar water.

The vapour mixture therefore contains a total of 2.8 kmols/hr.

At STP one mole of gas occupies 22.4 dm^3 hence 2.8 kmols would occupy 62.72 m^3.

However, the temperature of the vapour mixture may be as high as 200^oC. At constant pressure,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Therefore,

$$V_2 = \frac{62.72 \times 473}{273}$$

$V_2 = 108\ m^3/hr$

The partial condenser on reactor 6 consists of 131 tubes of 2.54 cm internal diameter. Hence the cross-sectional area available for flow can be calculated:

$$A = \frac{\pi \times (0.0254)^2}{4} \times 131$$

$$A = 0.07\ m^2$$

velocity = Q/A = 108/0.07 = 1542.09 m/hr = 0.43 m/s

This is insufficient to cause any problems with physical carryover.

Reactor 7

The volumetric vapour flowrate at 200°C is used to establish the linear velocity through the column.

Over a period of 1 hr V = 301.4 kg of which;

123.6 kg = Propylene glycol (1.63 kmol)
177.8 kg = Water (9.9 kmol)

1 mole of gas occupies 22.4 dm^3 at STP. Hence assuming no interaction of molecules the volume of the above gas would be 258.3 m^3. Hence, at 200°C;

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{258.3 \times 473}{273} = 447.5 \text{ m}^3$$

The packed column on reactor 7 has an internal diameter of 0.55m, thus, the cross-sectional area allowing for packing is:

$$A = 0.6 \times \pi \frac{0.55^2}{4} = 0.14 \text{ m}^2$$

Hence, the vapour velocity:

$$v = \frac{447.5}{0.14} = 3196 \text{ m/hr} = 0.9 \text{ m/s}$$

This velocity is also too low to cause problems of physical carryover of liquid.

APPENDIX E

Investigation into the Suitability of the Available Heat Exchanger for Use as the Partial Condenser for Reactor 5

E.1 Heat Load Calculations for the Reactor 5 Partial Condenser

Assumptions:

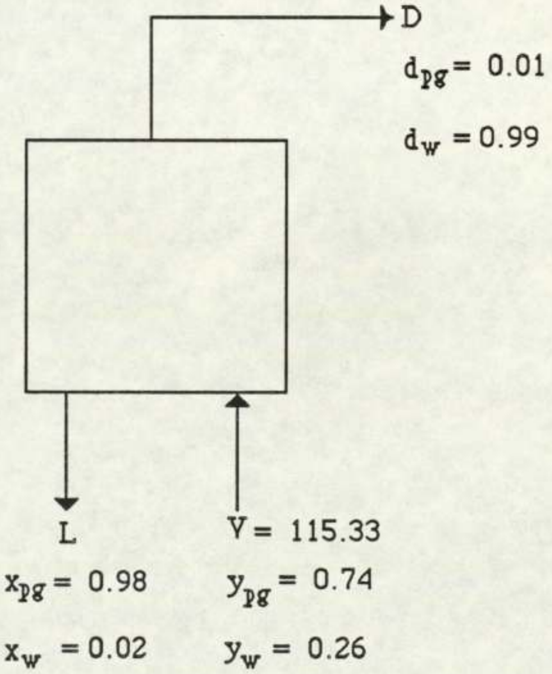
1 Top product is removed at T = 102°C and has equilibrium composition (99% water, 1% propylene glycol by mass).

2 Vapour stream flowrate and composition used are those calculated in Appendix C (flowrate = 115.33 kg/hr, composition = 74% propylene glycol and 26% water by mass).

3 Bottom product composition is based initially on equilibrium data and is assumed to be unchanged from initial calculation.

Basis 1 hour, all compositions given as mass fractions.

Figure E.1 Mass Balance Over Reactor 5 Overhead System



Overall balance:

$$V = L + D \qquad \text{E.1}$$

Balance on water

$$V y_W = L x_W + D d_W \qquad \text{E.2}$$

Substituting from E.1

$$V y_W = L x_W + (V-L)\, d_W$$

Rearranging

$$L = \frac{V(y_w - d_w)}{(x_w - d_w)}$$

$$L = 86.79$$

Hence,

$$D = 28.54$$

Assume the worst case for heat load calculations, ie. all separation occurs in the partial condenser.

Vapour enters the partial condenser at 200°C.

Vapour leaves the partial condenser at 102°C.

Calculation of dewpoint to final temperature at which initial composition vapour starts to condense.

Composition of initial vapour.

	Mass fraction	Molar fraction
Water	0.26	0.6
Propylene Glycol	0.74	0.4

$$K_i = \frac{P_i}{P} \qquad \text{E.3}$$

where,

K_i = equilibrium constant of component i at specified temperature

P_i = vapour pressure of component i at specified temperature

P = total pressure of system.

At dew point;

$$\Sigma x_\iota = \sum \frac{y_i}{K_i} = 1$$

Where x_i and y_i are mole fractions:

At T = 163°C.

P_W = 5031.2 mm Hg

P_{pg} = 331.4 mm Hg.

Hence,

$$K_w = \frac{5031.2}{760} = 6.62$$

$$K_{pg} = \frac{331.4}{760} = 0.436$$

$$\Sigma x_\iota = \frac{0.4}{0.436} + \frac{0.6}{6.620} = 1.008$$

Hence condensation starts at 163°C and continues until the vapour leaves the reactor at 102°C. Between 200°C and 163°C only cooling of the vapour takes place. The heat load for this will be considered later.

In order to consider the heat removal rate required for the partial condensation it is necessary to split the overall condensation range into zones. For each zone it is necessary to know the ratios of vapour to liquid entering and leaving. In the case of the Reactor 5 partial condenser, the condenser is vertical with vapour entering from the bottom. Hence it can be assumed that no subcooling of the liquid takes place.

It was decided to split the condensing range into three zones as follows:

Zone 1 - T = 163°C - 155°C
Zone 2 - T = 155°C - 130°C
Zone 3 - T = 130°C - 102°C

Zone 1 - Temperature Range = 163-155°C

Partial pressures at 155°C

$P_W = 4109$ mm Hg

$P_{pg} = 245$ mm Hg

Equilibrium constants at 155°C:

$$K_w^{155} = \frac{4109}{760} = 5.406$$

$$K_{pg}^{155} = \frac{245}{760} = 0.322$$

Expressing flowrates in terms of moles:

Let Y = vapour into zone

V = vapour out of zone

Y = 2.789 kmol/hr

$Y_{pg} = 1.123$ kmol/hr

$Y_W = 1.666$ kmol/hr.

Try an exit vapour/liquid ratio (V/L) of 3.75

Component	Y_i	K_i	$K_i(V/L)$	$1 + K_i(V/L)$	$L_i=Y_i/[1 + K_i(V/L)]$
Propylene glycol	1.123	0.322	1.208	2.208	0.509
Water	1.666	5.406	20.273	21.273	0.078
Total	2.789				0.587

V = Y-L

V = 2.789 - 0.587 = 2.202

$(V/L)_{calc} = 3.751$

Hence streams leaving zone 1 area as follows;

Liquid returning to reactor,

0.509 kmols of propylene glycol
0.078 kmols of water.

Vapour entering zone 2:

Propylene glycol = 1.123 - 0.509 = 0.614 kmols
Water = 1.666 - 0.078 = 1.588 kmols

Zone 2 - Temperature Range = 155 - 130°C

Partial Pressures at 130°C
$P_W = 2031$ mm Hg
$P_{pg} = 93$ mm Hg.

Equilibrium constants at 130°C

$$K_w^{130} = \frac{2031}{760} = 2.672$$

$$K_{pg}^{130} = \frac{93}{760} = 0.122$$

V/L = 1.9

Component	Y_i	K_i	$K_i(V/L)$	$1 + K_i(V/L)$	$L_i=Y_i/[1 + K_i(V/L)]$
Propylene glycol	0.614	0.122	0.23	1.232	0.498
Water	1.588	2.672	5.077	6.077	0.261
Total	2.202				0.759

V = Y-L
V = 2.202 - 0.759 = 1.443

$(V/L)_{calc} = 1.901$

Streams leaving zone 2 are as follows:

Liquid returning to reactor

0.498 kmoles propylene glycol

0.261 kmoles water

Vapour entering zone 3

Propylene glycol = 0.614 - 0.498 = 0.116 kmols

Water = 1.588 - 0.261 = 1.327 kmols

Zone 3 - Temperature Range = 130 - 102°C

Partial pressures at 102°C

P_w = 818 mm Hg

P_{pg}= 26 mm Hg.

Equilibrium constants at 102°C

$$K_w^{102} = \frac{818}{760} = 1.076$$

$$K_{pg}^{102} = \frac{26}{760} = 0.034$$

V/L = 0.31

Component	Y_i	K_i	$K_i(V/L)$	$1 + K_i(V/L)$	$Li=Y_i/[1 + K_i(V/L)]$
Propylene glycol	0.116	0.034	0.011	1.011	0.115
Water	1.327	1.076	0.344	1.344	0.987
Total	1.443				1.102

V = Y-L

V = 1.443 - 1.102 = 0.341

$(V/L)_{calc}$ = 0.309

Streams leaving zone 3 are as follows:

Liquid returning to reactor
Propylene glycol = 0.115 kmoles
Water = 0.987 kmoles

Vapour leaving partial condenser
Propylene glycol = 0.116 - 0.115 = 0.001 kmoles
Water = 1.327 - 0.987 = 0.340 kmoles

Overall Mass Balance (Revised)

Vapour in = 1.123 kmoles propylene glycol
= 1.666 kmoles water
Liquid out = L1 + L2 + L3
Water content = 0.078 + 0.261 + 0.987 = 1.326 kmoles
Propylene glycol content = 0.509 + 0.498 + 0.115 = 1.122 kmols

Vapour out
Water content = 0.340 kmoles
Propylene glycol content = 0.001 kmols

E.2 Heat Load Calculations for Partial Condenser

Zone 0: Cooling of vapour from 200°C to dew point at 163°C

Enthalpy:
Steam at 200°C hv = 2791 kJ/kg
Steam at 163°C hv = 2760 kJ/kg

No data was available for the enthalpy of propylene glycol vapour. Therefore the enthalpy of the vapour was assumed to be equal to the enthalpy of the liquid plus the latent heat of vapourisation. At T = 200°C the vapour is assumed to have the same specific heat as at the boiling point.

Propylene glycol at 200^oC

hv = 693 + 712 = 1405 kJ/kg

Propylene glycol at 163^oC

hv = 541 + 758 = 1299 kJ/kg

Component	Y_i	h_v^{200} (kJ/kg)	H_v^{200} (MJ)	h_v^{163} (kJ/kg)	H_v^{163} (MJ)
Propylene glycol	1.123	1405	120	1299	111
Water	1.666	2791	84	2760	83
Total			204		194

where,

h_i^t = enthalpy of component i at temperature t ^oC, kJ/kg

H_i = Total enthalpy of component i, MJ

nb 0^oC is used as the datum temperature for all calculations

Q = ΔH = 10 MJ

Zone 1: Temperature range = 163 - 155^oC

Specific heats

Propylene glycol liquid at 155^oC,	h_L = 507 kJ/kg
Propylene glycol vapour at 155^oC,	h_V = 1267 kJ/kg
Steam at 155^oC,	hv = 2751 kJ/kg
Water at 155^oC,	h_L= 654 kJ/kg

Heat in from zone 0 = 194 MJ

Heat out of zone 1

	Vapour			Liquid		
Component	Y_i	h_V (kJ/kg)	H_V (MJ)	L_i	h_L (kJ/kg)	H_V (MJ)
Propylene glycol	0.614	1267	59	0.509	507	20
Water	1.588	2751	79	0.078	654	1
Total			138			21

$Q = \Delta H = 194 - (138 + 21)$

$= 35$ MJ

Zone 2: Temperature range = 155^{o}C - 130^{o}C

Specific heat

Propylene glycol vapour at 130^{o}C, $h_V = 1194$ kJ/kg

Propylene glycol liquid at 130^{o}C, $h_L = 407$ kJ/kg

Steam at 130^{o}C, $h_V = 2720$ kJ/kg

Water at 130^{o}C, $h_L = 546$ kJ/kg

Heat from Zone 1 = 138 MJ.

Heat out of Zone 2

		Vapour		Liquid		
Component	Y_i	h_V (kJ/kg)	H_V (MJ)	L_i	h_L (kJ/kg)	H_V (MJ)
Propylene glycol	0.116	1194	11	0.498	407	15
Water	1.327	2720	65	0.261	546	3
Total			76			18

$Q = \Delta H = 44$ MJ

Zone 3: Temperature range = 130 - 102^{o}C

Specific heats

Propylene glycol vapour at 102^{o}C, $h_V = 117$ kJ/kg

Propylene glycol liquid at 102^{o}C, $h_L = 302$ kJ/kg

Steam at 102^{o}C, $h_V = 2681$ kJ/kg

Water at 102^{o}C, $h_L = 428$ kJ/kg

Heat in from Zone 2 = 76 MJ

Heat out of zone 3

	Vapour			Liquid		
Component	Y_i	h_V (kJ/kg)	H_V (MJ)	L_i	h_L (kJ/kg)	H_V (MJ)
Propylene glycol	0.001	1117	0	0.115	302	3
Water	0.340	2681	16	0.987	428	8
Total			16			11

$Q = \Delta H = 76 - (16 + 11) = 49$ MJ.

Table E.1 Overall Heat Transfer Across Reactor 5 partial Condenser

Assume that cooling water enters at 20^{o}C and leaves at 35^{o}C.

Zone	T_V (^{o}C)	Q (MJ)	Δt_W	t_W	Δt_{av}	$Q/\Delta t$
0	200			35		
	163	10	1.1	33.9	147.0	0.07
1	155	35	3.8	30.1	127.0	0.28
2	130	44	4.8	25.3	114.8	0.38
3	102	49	5.3	20	93.4	0.52
Total		138	15			1.25

$Q = mC_p \Delta T$

$C_p = 4.181$ kJ/kg^{o}C (at 30^{o}C)

Hence,

$$m = \frac{138 \times 10^3}{4.181 \times 15} = 2200 \text{ kg/hr}$$

For each zone use

$$\Delta t_w = \frac{Q}{mC_p} = \frac{Q}{9200}$$

$$\text{Weighted } \Delta t = \frac{\Sigma Q}{\Sigma UA} = 110.4^{\circ}\text{C}$$

E.3 Calculations to Determine the Suitability of the Available Heat Exchanger for use as the Partial Condenser on Reactor 5

The heat exchanger available for use has an internal shell diameter of 39 cm. It contains 91 tubes of 2.5 cm outside diameter constructed of 16 swg steel on a 3.2 cm triangular pitch. The tube length is 91 cm.

Shell-side Heat Transfer Coefficient

Area available for flow = A_s

$$A_s = \frac{ID \times C'B}{P_t}$$

ID = internal diameter of shell = 0.39 m

C' = clearance between tubes = 0.006 m

B = baffle spacing (no baffles hence 0.91 m)

P_t = tube pitch = 0.032 m.

$A_s = 0.07\ m^2$

W = water flowrate = 2200 kg/hr

$$G_s = \frac{W}{A_s} = 31\,430\ kg/hr\ m^2$$

Assume properties of water at T = 27.5°C.

μ = viscosity =0.86 cp = 3.1 kg/m hr

C_p = specific heat capacity, = 4.40 kJ/hr m^2 °C

k = thermal conductivity = 2.23 kJ/hr m °C

De = equivalent diameter = (4 x axial flow area/wetted perimeter) = 0.018 m

Calculate the shell-side Reynolds number.

$$Re_s = \frac{DeG_s}{\mu} = 182$$

From the correlation referred to in Chapter 7, $j_H = 8.2$

Assuming negligible viscosity change over small temperature changes:

$$j_H = \frac{h_o D_e}{k} \times \left(\frac{C_p \mu}{k}\right)^{-1/3}$$

Hence, the shell-side heat transfer coefficient, h_o, can be calculated:

$h_o = 555$ kJ/hr m^2 °C

The Tube-Side Heat Transfer Coefficients

Consider the tube-side in two separate stages. The first stage is the desuperheating stage where the vapour is cooled from 200°C to 163°C. The second stage is where condensation occurs and uncondensed vapour leaves at 102°C.

Stage 1 - The Desuperheating Section

The maximum flowrate through the tubes is extremely low. For this reason it is considered unlikely for a continuous liquid film to be formed on the tube walls. It has been assumed for the purposes of these calculations that desuperheating occurs via a vapour film.

In the absence of any available information about the properties of propylene glycol as a vapour, it has been assumed that the vapour has the properties of steam at the appropriate temperature. Assume that the vapour to be desuperheated has the physical properties of steam at 180°C.

$C_p = 1.9$ kg/kJ °C
$\mu = 0.05$ kg/m hr
$k = 0.1$ kJ/hr m °C

G = mass velocity through the tubes
W = mass flow = 115.33 kg/hr
D = internal diameter of tubes = 0.02 m
Nt = number of tubes = 91

a_t = flow area through tubes

$$a_t = \frac{N_t \pi D^2}{4} = 0.03 \text{ m}^2$$

$$G = \frac{W}{a_t} = 3844 \text{ kg/hr m}^2$$

Calculating the tube-side Reynolds number.

$$Re = \frac{DG}{\mu} = 1538$$

The ratio of tube length to internal diameter = 41.4. From the correlation(12),

$j_H = 7$

where,

$$j_H = \frac{h_i D}{k}\left[\frac{C_p \mu}{k}\right]^{1/3}$$

hence,

h_i = 34.3 kJ/hr m °C

The overall clean heat transfer coefficient can be now calculated:

$$U_C = \frac{h_i h_o}{h_i + h_o}$$

U_C = 32.2 kJ/hr m^2 °C

The heat transferred in the desuperheating section = 10 MJ/hr

Water temperatures:

t_{in} = 33.9 °C

t_{out} = 35 °C

Vapour temperatures:

$T_{in} = 200\ ^oC$

$T_{out} = 163\ ^oC$

Calculating the logarithmic mean temperature difference:

$$\Delta T_m = \frac{(T_{out} - t_{out}) - (T_{in} - t_{in})}{Ln\left[\frac{(T_{out} - t_{out})}{(T_{in} - t_{in})}\right]}$$

$\Delta T_m = 146\ ^oC$

$Q = UA\Delta T_m$

Hence,

$$A = \frac{Q}{U\Delta T_m} = 2.12\ m^2$$

<u>Stage 2 - The Condensing Section</u>

As previously mentioned, it has been calculated that there is insufficient condensate to form a continuous film on the inside of the tubes. However, since filmwise condensation is far less efficient than dropwise condensation, it has been assumed that a liquid film does exist in the condensing section of the heat exchanger. The film is assumed to have the properties of propylene glycol since this is the least volatile of the components.

Assume $h_c = 4088$ kJ/hr $m^2\ ^oC$ and average vapour temperature = 132 ^oC.

hence, $t_w = 119\ ^oC$

and,

$$t_f = \frac{132 + 119}{2} = 125\ ^oC$$

Assume film has properties of propylene glycol at 120 ^{o}C

μ_f = 8.28 kg/m hr
k_f = 0.6 kJ/hr m ^{o}C
ρf = 1020 kg/m^3

Condensing load,

$$G' = \frac{W}{\pi N_t D} = 20.2 \text{ kg/hr}$$

The condensing load can be correlated against the physical properties of the film to give the heat transfer coefficient of condensation(12).

h_c = 6337 kJ/hr m^2 ^{o}C

Using this to recalculate the temperature of the film:

t_w = 123 ^{o}C

Recalculating the film temperature,

$$t_f = \frac{123+132}{2} = 127.5\ ^{o}\text{C}$$

The slight change in film temperature is unlikely to significantly effect the physical properties of the film. Therefore, it is not necessary to recalculate the heat transfer coefficient.

The overall heat transfer coefficient of stage 2 can now be calculated.

$$U_C = \frac{h_c h_o}{h_c + h_o} 510 \text{ kJ/hr m}^2\ ^{o}\text{C}$$

The logarithmic mean temperature difference for the condensing section of the heat exchanger can now be calculated.

Water temperatures:

$t_{in} = 20\ ^{o}C$

$t_{out} = 33.9\ ^{o}C$

Vapour temperatures:

$T_{in} = 163\ ^{o}C$

$T_{out} = 102\ ^{o}C$

$$\Delta T_m = \frac{(163 - 33.9) - (102 - 20)}{\ln\left[\frac{163 - 33.9}{102 - 20}\right]} = 104\ ^{o}C$$

Heat load over the condensing area,

Q = 128 MJ/hr.

Hence, the necessary heat transfer area can be calculated.

$$A = \frac{Q}{U_C \Delta T_m} = 2.4\ m^2$$

The total heat transfer area required to produce the necessary degree of desuperheating and condensation is, therefore, $2.12 + 2.4 = 4.62\ m^2$.

The heat transfer on the available exchanger is;

$$\pi D N_t L = 5.2\ m^2$$

Hence the available heat exchanger has sufficient heat transfer area for the purpose. There is also an excess area of 12.5 % to allow for dirt and scaling.

APPENDIX F

Calculations of Mass Transfer Coefficients at the Middle and the Top of the Packed Column

Conditions at the Centre of the Packed Column

ρ'_L = 60.57 lb /ft^3
ρ'_v = 0.1027 lb /ft^3
μ''_v = 0.027 lb /ft hr
μ''_L = 2.66 lb /ft hr
σ' = 46 dynes/cm
D_V = 2.9×10^{-8} ft^2/hr
D_L = 8.41×10^{-5} ft^2/hr

Flowrates

V' = 642.6 lb/ft^2hr
L' = 429.2 lb/ft^2hr
V'_m = 23.57 lb moles /hr ft^2.
L'_m = 12.13 lb moles /hr ft^2.

The constants for equation 7.15 are;
m = 8,200.
n = $3.15 * 10^{-4} L^1 - 0.30 = -0.165$.
p = - 1.04.

V'_{mod} = 549.14 lb/ft^2hr
A_{aw} = 5.29 ft^2 /ft^3 packed volume.

Repeating the holdup calculations, the following results are obtained:

ϕ_{tw} = 0.0494.
ϕ_{sw} = 0.0325
ϕ_{ow} = 0.0169
ϕ_s = 0.0208
H = 1.361

ϕ_o = 0.0230
A_a = 7.200 ft^2/ft^3
ϕ_t = 0.0438
e_o = 0.7962
Sc_V = 0.709.

Hence,
k'_V = 1.478 lb moles/hr ft^2 = k'_y

Liquid Phase Coefficients:

Sc_L = 522.5
k_L = 2.271 lb moles/hr ft^2 (lb moles/ft^3)
ρ'_m = 2.054 lb moles/ft^3
k'_x = 4.665 ld moles/ft^2

Conditions at the Top of the Column

The vapour and liquid streams are assumed to have the properties of steam and water, respectively, at 105°C.

Physical Properties
ρ'_L = 59.60 lb /ft^3
r'_V = 0.044 lb /ft^3
μ''_V = 0.03 lb /ft hr
μ''_L = 0.58 lb /ft hr
σ' = 59 dynes/cm
D_V = 2.72×10^{-8} ft^2/hr
D_L = 3.61×10^{-4} ft^2/hr

Flowrates
V' = 425.2 lb/ft^2hr
L' = 212.7 lb/ft^2hr

V'_m = 22.88 lb moles /hr ft^2.
L'_m = 11.44 lb moles /hr ft^2.

The constants for equation 7.15 are;

m = 8,200.
n = 0.233
p = - 1.04.

V'_{mod} = 555.1 lb/ft^{2}hr
A_{aw} = 7.137 ft^2 /ft^3 packed volume.

ϕ_{tw} = 0.0392.
ϕ_{sw} = 0.0324
ϕ_{ow} = 0.0068
ϕ_s = 0.0259
H = 2.572
ϕ_o = 0.0175
A_a = 18.354 ft^2 /ft^3
ϕ_t = 0.0434
e_o = 0.7966
Sc_V = 1.96

Hence,
k'_V = 1.367 lb moles/hr ft^2 = k'_y

Liquid Phase Coefficients:

Sc_L = 26.97
k_L = 3.205 lb moles/hr ft^2 (lb moles/ft^3)
ρ'_m = 3.315 lb moles/ft^3
k'_x = 10.626 lb moles/ hr ft^2

APPENDIX G

Design of the Partial Condenser for Packed Column System

The partial condenser is specified as containing 36 tubes, 16 swg stainless steel, 1.9 cm outside diameter, on a 2.4 cm triangular pitch. The internal diameter of the shell is 20.3 cm.

Condensation takes place on the tube-side. It is assumed that the tube-side temperature is maintained 105°C and that the vapour and condensate have the properties of steam and water, respectively.

Assume a 10°C temperature difference of the cooling water and countercurrent flow of the cooling water through the shell.

Water Side Calculations

assume, $t_{in} = 20^oC$

$t_{out} = 30^oC$

$\Delta t_W = 10^oC$

C_p = specific heat capacity of water = 4.1868 kJ/kg^{o}C

M = mass flowrate of water, kg/hr

Total Heat Load = Q = 114 MJ/hr

and, $Q = MC_p\Delta t_W$ - G.1

Hence, M =2725 kg/hr

Finally, the log mean temperature difference across the condenser can be calculated.

LMTD = 80°C.

Shell-side Heat Transfer Coefficient

A_s = Heat transfer surface area for subcooling on water side, m^2

$$A_s = \frac{ID \times C'B}{P_t} \qquad - G.2$$

$ID =$ internal diameter of shell = 0.204 m

$C' =$ clearance between tubes = 0.0048 m

$B =$ baffle spacing = 0.30 m

$P_t =$ tube pitch = 0.024 m

$A_s = 0.012 \, m^2$

$G_s =$ mass velocity of cooling water, kg/hr m^2

$=$ 227 083 kg/hr m^2

$t_a =$ average shell-side temperature = 25 ^oC

$\mu =$ 0.86 cp = 3.1 kg/m hr

j_H = Factor for Heat Transfer, based on the physical properties of the cooling water at its average temperature (25^{o}C), and the shell side Reynolds Number Re_s, correlation from Kern$^{(12)}$.

$$j_H = \frac{h_o D_e}{k} \times \left(\frac{C_p m}{k}\right)^{-1/3} \times \left(\frac{\mu}{\mu_w}\right)^{-0.14} \qquad - G.3$$

where,

h_o = heat transfer coefficient for outside fluid, kJ/hr m^2 ^oC

D_e = equivalent diameter for heat transfer and pressure drop

= 0.015 m

k = thermal conductivity, = 2.23 kJ/hr m ^oC

C_p = specific heat capacity, = 4.60 kJ/hr m^2 ^oC

μ_w = viscosity at wall temperature, assume unchanged.

= 3.1 kg/m hr

$$Re_s = \frac{D_e G_s}{\mu} = 1099$$

From correlation, $j_H = 17$

hence, $h_o = 4526$ kJ/hr m^2 ^oC

Tube-side Heat Transfer Coefficient

From the heat balance in Chapter 7;

$Q = 114 \times 10^3$ kJ/hr

T_v = vapour temp = 105 ^oC

It is possible to calculate the tube wall temperature by estimating the internal heat transfer coefficient, h_{io}, using equation 7.9:

Assume h_{io} = 37 000 kJ/hr m^2 ^oC

Hence, t_w = 96 ^oC. Assume the liquid film on the inside of the tubes has the properties of water at 96 ^oC.

μ_f = 0.98 kg/m hr
k_f = 2.45 kJ/hr m ^oC
ρ_f = 960 kg/m^3
g = gravitational constant due to acceleration, = 127×10^3 m/hr^2.
L_c = condensate loading for vertical tubes, kg/hr m

$$L_c = \frac{L}{P\ N_t D}$$

L = total mass flowrate of condensate,
= 52.6 kg/hr

N_t = number of tubes in heat exchanger, = 36
D = internal diameter of tubes, = 0.016 m
L_c = 29 kg/hr m

The tube side Reynolds Number, Re_t, can now be calculated:

$$Re_t = \frac{4L_c}{\mu_f} = 118$$

The average value of the condensing film heat transfer coefficient can be estimated from the Reynolds Number using the correlation of Colburn(18).

$$h_{av} = 0.38 \left(\frac{\mu_f^2}{k_f^3 \rho_f^2 g} \right)^{1/3} \qquad G.3$$

$$h_{av} = h_i = 46\ 160 \text{ kJ/hr m}^2\ {}^oC$$

This value can now be adjusted for wall thickness by multiplying by the ratio of the internal to external diameters:

$$h_{io} = \frac{0.0016}{0.0019} \times 46\ 160 = 38\ 157 \text{ kJ/hr m}^2\ {}^oC$$

This compares reasonably well with the assumed value of 37000 kJ/hr m^2 ^oC. To check, the tube wall temperature can be recalculated using the amended heat transfer coefficient. This gives a wall temperature of 96.5^{o}C. Consequently, changes in physical properties due to increased temperature are not significant.

The Clean Overall Heat Transfer Coefficient can now be calculated from equation 7.12:

$$U_C = \frac{h_{io} h_o}{h_{io} + h_o}$$

$U_C = 4046$ kJ/hr m^2 ^{o}C

Dirt Factors

The following dirt factors have been assumed:

Rd_o = external coefficient, cooling water from cooling towers = 5×10^{-5}
Rd_i = internal coefficient, condensing vapours = 1×10^{-4}

Hence, overall coefficient, $Rd = 1.5 \times 10^{-4}$

$$\frac{1}{U_D} = \frac{1}{U_C} + Rd$$

$U_D = 2518$ kJ/hr m^2 ^{o}C

The actual required tube length, L_t, can now be calculated.

$$A = \frac{Q}{U_D \, \Delta T_{av}} = 0.6 \text{ m}^2$$

and,

$$L_t = \frac{A}{P \; D \, N_t} = 0.33 \text{ m}$$

In order to ensure that the condenser was adequately designed to cope with any fluctuations of flow over and above the calculated maximum flowrate, it was decided to increase the tube length to 0.45 m. No baffles are considered necessary for such a short tube length.

Pressure Drop Calculations

It has been necessary to calculate the pressure drop on both the shell- and the tube-side using Imperial units because of the correlation available.

Shell side Pressure Drop

The shell side Reynolds Number = 1099.

From Kern(12), this corresponds to a friction factor of 0.003 ft^2/in^2.

The pressure drop can now be calculated from equation G.4:

$$L_t = \frac{A}{P \ D N_t} = 0.33 \text{ m} \qquad \text{- G.4}$$

where,

Δp_S = shell side pressure drop, psi

G' = mass velocity of cooling water = 46 500 lb/hr ft^2

Ds = internal diameter of shell = 0.667 ft

N = number of baffles = 0

g' = gravitational constant = 4.17×10^8 ft/hr^2

ρ'_s = density of cooling water = 62.45 lb/ft^3

De = equivalent diameter = 0.05 ft

$\phi_s = \mu/\mu_w$, assume = 1

Hence, Δp_S = 0.002 psi = 11.5 N/m^2

Tube Side Pressure Drop

The tube side Reynolds Number = 119. From Kern(12), this corresponds to a friction factor, f, of 0.0039. The pressure drop can now be calculated from equation G.5:

$$\Delta p_t = \frac{1}{2}\frac{fG'^2_t L' n}{5.22 \times 10^{10} D_t} \qquad \text{- G.5}$$

where,

Δp_t = tube side pressure drop, psi

G_t' = tube side mass velocity, = 3073 lb/hr ft^2

L' = tube length = 1.5 ft

n = number of passes = 1

D_t = internal diameter of tube = 0.517 ft

Hence, $\Delta p_t = 1 \times 10^{-6}$ psi = 0.07 N/m^2