# COMPUTER CONTROL OF A BATCH PROCESS FOR RESIN MANUFACTURE

A Thesis Submitted for the Degree of

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by

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## SUMMARY

The aim of the project is to investigate the provision of automatic control for the batch reactors of the type presently used in industry for the production of butylated melamine formaldehyde resins.

For that purpose a pilot plant was built at Aston University that was interfaced with the Departmental Honeywell 316 Computer for data acquisition and control purposes. The computer control of the plant supplied an easy and effective way to operate the plant and shorter and more consistent batches were achieved.

A new design of the distillation system was used in the pilot plant and the operating data were compared with industrial data. A reaction model was developed to simulate the chemical changes of the resin during the process. The formulation of the reaction model and the experimental data from previous research supplied the necessary background for a scientific discussion of the functional groups involved in the reactions of the melamine resins. As a consequence, a deeper understanding of the process was achieved and the previously empirical operation procedure could be explained in a new perspective.

Further extensions of this work are recommended as regards the kinetic model, the plant and computer control.

Key Words:

Butylated melamine formaldehyde resins, computer control, distillation, batch reactor, process simulation.

# ACKNOWLEDGEMENTS

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DEDICATED TO

Sousan, my wife,

Sara, my daughter, and

Maria and Jaime, my parents.

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# CHAPTER ONE

# INTRODUCTION

## 1. INTRODUCTION

The work presented in this thesis is the outcome of a research project involving Aston University and B.I.P. Chemicals Limited. Two major components can be identified: the process and the computer control of the plant.

The process under consideration, is the manufacture of butylated melamine formaldehyde resins. In spite of resins of this kind having been produced for over 35 years the complexity of the chemical reactions involved and the difficulties encountered in analysing the products certainly contributed for the poor understanding of the chemistry involved in the process. The extensive experience in the field, and the apparent simplicity of the operational procedures involved made it possible to start industrial production and commercialisation of melamine resins at an early date. However, due to the empirical nature of the information available, it is not uncommon to obtain batches of products, which are off-specification. In order to avoid this kind of problem, it was decided to build a pilot plant at Aston University that adequately represents the large scale equipment in industry. The active participation of the author in the operation of the batch process, both in industry and laboratory, supplied the necessary experience for the operation of the pilot plant at Aston. The pilot plant can be seen as a batch process since it consists mainly of a batch reactor and a distillation apparatus for the removal of the water from the reactor. The distillation arrangement of the pilot plant is different from the one used in industry and it works in a more effective way.

The second component of the project involves the computer control of the process. The pilot plant was built with all the necessary instrumentation to be interfaced with the Departmental Honeywell 316 Computer for data acquisition and control purposes. The use control of the process considerably improved the product quality, and simplified the operation of the plant. More, the use of a computer for control purposes is a flexible method when compared to conventional analogue equipment since it permits the implementation of different types of control strategies without having to buy and install additional analogue controllers. The objectives of this work can be summarised as follows:

(1) To study the process by establishing a mathematical model that describes it adequately. The information for this model came from research previously done by B.I.P. and data from the open literature, and the variations of reaction product due to quality changes in new materials was ascertained.

(2) To study and implement the computer control of the process so that the right product specification is achieved at the end of the batch.

The thesis comprises the following chapters:

| | |
|---|---|
| Chapter 2 | Literature Survey - A critical review of all the relevant publications dealing with formaldehyde resins and in particular butylated melamine formaldehyde resins. |
| Chapter 3 | Industrial and laboratory processes. Description of the experience of the author in industry and laboratory environments with the technical information that influenced the Pilot Plant's construction and commissioning. |
| Chapter 4 | Kinetic model of the reactions involved in the manufacture of butylated melamine formaldehyde resins. Description of the model developed and comparison of the simulated results with the experimental data. |
| Chapter 5 | The Pilot Plant. Description of the pilot plant equipment including the instrumentation used and computer interface. |
| Chapter 6 | The operation of the Pilot Plant. Description of the operating procedure of the Pilot Plant and presentation of the Computer Program for the control of the process. |

| | |
|---|---|
| Chapter 7 | Experimental Results and Conditions. In this chapter a description of the experimental runs on the plant is presented together with the results obtained, discussion and conclusions. |
| Chapter 8 | Further Work. Several suggestions for further work are presented concerning the fields in which the author feels that further improvement might arise. |

# CHAPTER TWO

# LITERATURE SURVEY

The principal materials used in the manufacture of butylated formaldehyde-melamine resins are: melamine, butanol and formalin. Of the three main raw materials, formalin is the most difficult to characterise in terms of chemical structure. Melamine and butanol are available in almost pure form. Therefore, it was thought to be important to start the literature survey with a section on formaldehyde.

## 2.1 Formaldehyde

Formaldehyde is often assumed to be a simple chemical compound, but as used commercially is a whole series of compounds [2]. Walker [1] in his monograph on this subject gives size information on different forms of formaldehyde. In the United States the following forms are available: Formalin, aqueous solution containing 35-37% HCHO and 5-10% methanol, Paraformaldehyde, in flake form called Paraform and formaldehyde solutions in alcohols called Formals. The most common alcohols used are n-propanol, isobutanol, n -butanol and iso-n-butanol mixture [2]. In Britain the forms commercially available are formalin and the more expansive paraformaldehyde.

### 2.1.1 Formalin

Aqueous formaldehyde is usually 37 wt% formaldehyde though more concentrated solutions are available. Formaldehyde is present largely as an equilibrium mixture of methylene glycol and low weight polyoxymethylene.

glycols in aqueous solution, and the unhydrated formaldehyde monomer is less than 0.1% in the solution (6). The equilibrium in aqueous solutions can be represented by the following reaction scheme:

$HCHO + H_2O \rightleftharpoons HO\ CH_2\ OH$ - Formation of Hemiformal

$HOCH_2OH + HO\ (CH_2O)_{n-1} \rightleftharpoons HO(CH_2O)_n\ H + H_2O$ - Polymerisation of polyoxymethylene glycols.

The presence of hemiformal was proved by Infrared spectrocopy by Tsuge et alia (7) and by Nuclear Magnetic Resonance (NMR) (8, 9, 10). Formalin can be supplied in two forms: unstabilized or methanol-stabilized (3). The latter may be stored at room temperature without precipitation of solid formaldehyde polymers because it contains 5-10% of methyl alcohol. The uninhibited type must be maintained at a temperature of at least $32^{o}C$ to prevent the separation of solid formaldehyde polymers. The addition of methanol to formalin promotes methanolysis and subsequent depolymerization of polyoxymethylene glycol homologues as follows:

$HO(CH_2O)_nH + CH_3\ OH \rightleftharpoons HO(CH_2O)_{n-1} + CH_3\ OCH_2OH$

$HO(CH_2O)_{n-1}H + CH_3OCH_2OH \rightleftharpoons HO(CH_2O)_{n-2}H + CH_3O(CH_2O)_2H$

The weak I.R absorption band at 1190 $cm^{-1}$ for the aqueous formaldehyde solution to which methanol was added was assigned to $CH_3$ vibration of terminal methyl group (7). The formation of hemiformal was confirmed by Hydrogen NMR under acidic and alkaline conditions by

Hamano et alia in 1980 [11].

Recently, many papers have been published on the average degree of polymerization ($P_n$) and molecular species distribution in formalin solutions. $P_n$ was calculated for low molecular weight polyoxymethylene glycols by different methods. Infrared spectroscopy was also used together with end group analysis [12] and gel permeation chromatography [13]. The value obtained by GPC is lower than expected, because of the depolymerization of polyoxymethylene glycols in tetrahydrofuran (THR) as eluting solvent. Dankelman and Daeman [8] determined by $^1$H-MNR the molecular species distribution of polyoxymethylene glycols up to heptamer in formalin using silylation pretreatment of formalin with N,O-bis (trimethyl silyl) trifluoroacetamide (BSTFA) followed by gas chromatography on a chromosorb w column.

| | Relative Mole % | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $HO(CH_2O)_n H$ | | | | | | | $CH_3O(CH_2O)_nH$ | | | Free MeoH |
| n | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 1 | 2 | >3 | |
| 37% formalin + 8% methanol | 5.1 | 8.9 | 6.7 | 2.7 | 1.4 | 0.6 | 0.3 | 7.8 | 5.2 | 5.7 | 0.8 |
| 37% formalin + 14% methanol | 5.0 | 7.1 | 4.2 | 1.3 | 0.8 | - | - | 13.4 | 8.6 | 8.8 | 1.7 |

Table 2.1 - Distribution of Polyoxymethylene glycols and hemiformals in formalin at room temperature, as determined by GC and 1H-NMR [8]

Assuming that $P_n$ of polyhemiformals is 3, the value of $P_n$ calculated for table 2.1 is 2.3 for the sample containing 8% methanol, and 2.0 for that containing 14% methanol.

Three signals of polyoxymethylene glycol for $P_n = 1, 2$ and > 3 could be observed separately in neutral or acidic solution by $^1H$-NMR [8, 9, 14, 15] and four signals with $P_n = 1, 2, 3$ and > 4 in $D_2O$ [16]. Each oligomer with $P_n =$ 1, 2 and > 3 in hemiformals could be determined by $^1H$-NMR on the basis of terminal methyl protons [8].

Polyoxymethylene glycols in formalin can be separated by $^{13}C$-NMR using $C_1$ carbon signal for $P_n = 1$-$3$, $C_2$ carbon signal for $P_n = 4$ and $C_3$ carbon signal for $P_n > 5$ [10, 16, 17, 18].

$$HOCH_2OCH_2OCH_2OCH_2O.....CH_2OH$$

1 2 3

$C_1$ carbon and terminal carbon signals were used for determination of $P_n = 1, 2$ and 3 groups in polyhemiformals.

The gel permeation chromatogram of formalin containing some precipitate showed two separate peaks [13]. A value of $P_n$ calculated for the peak with lower elution count was about 10.

### 2.1.2 Paraformaldehyde

Paraformaldehyde is a mixture of polyoxymethylene glycols, $HO(CH_2O)_nH$ (I) and $CH_3O(CH_2O)_nH$ (II) with n from 7 to as much as 100. It is commercially available as a powder (95%) and as flake (91%). Paraformaldehyde is an unstable polymer that easily regenerates formaldehyde in solution. The way the polymer chain is broken depends on the pH of the medium. In alkaline conditions the chains depolymerize from the ends, whereas in acid solution the chains are randomly cleared [1].

Some literature is available about methods to measure the average degree of polymerisation ($P_n$). The $P_n$ value can be obtained from a linear relationship between the ratio of the absorption intensity of OH stretching vibration band to that of CH stretching vibration band and the ratio of hydroxyl group to that of carbon in normal aliphatic alcohols as artificial standards [19]. The pyrolysis gas chromatographic determination of paraformaldehyde is based on the fact that 1 mole of oligomer (I) produces 1 mole of water and 1 mole of oligomer (II) produces 1 mole methanol [20, 21].

### 2.1.3 Comparison of the use of Different Forms of Formaldehyde

Comparing the two forms of formaldehyde available in this country it is clear that paraformaldehyde is the easiest to use in the manufacture of butylated formaldehyde melamine resins, taking into account that there are few more unpleasant jobs than pouring formalin out of large drums for intermittent resin manufacture. Formalin has however the advantage of being cheap. In this work formalin has been used, stabilized with 7% of methanol. Whilst formalin is the most economical source of formaldehyde for resin manufacture its properties make it absolutely essential to have adequate facilities for its storage, handling and measurement.

The first run done in the pilot plant at Aston University formalin was not properly stored. It was left four days below 60°F. As a result some precipitation occur and the resin manufactured was completely out of specification. Its viscosity was too high and gelation nearly occur in the reactor. Special care should therefore be given to the storage and handling of formalin. In the United States formaldehyde alcohol solutions are also used. They are mixtures of the hemi-acetals of monomeric and polymeric formaldehyde with the alcohol employed. They do not precipitate polymers nor require warm storage to maintain stability. In using different forms of formaldehyde in the manufacture of amino resins. it is necessary to adjust the processes for the effects of different amounts of water to be eliminated and different reactivity of the materials.

## 2.2 History and Applications of Amino Plastics

The manufacture of amino plastics and the theoretical background of the chemistry involved has been referred to as "the world of strange processes control cycles and batch processes reminiscent of 18th century cottage industry". This is, of course, a very exaggerated way of looking at the matter, but this view rather illustrates the fact that rapid commerical development of the resin technology has far outdistanced the capability to analyse the products. That is maybe the reason why many literature contributions and patents can be found that describe how to produce a resin with a certain number of properties but publications on kinetics and mechanisms of the reactions involved in the process are rather scarce. The thermosetting resins derived from the reaction of formaldehyde with urea and melamine are often referred to as the amino plastics. This class of plastics also includes resins formed by reaction of other aldehydes, such as acetaldehyde or furfuraldehyde with other bases like phenol, guaridine, aniline and so on. Perhaps the first research on the reaction of formaldehyde with amide hydrogens was done by Tollens [69] in 1884. He isolated a compound monomethylol urea, the simplest addition product. Further research by Einhorn and Hamberger led to the isolation and identification of dimethylolurea [70].

Industrial interest was, however, aroused much later with the registration of a patent by Dutchman and Hanns John in 1918 [71]. The growth of the urea-formaldehyde resin industry in the twenties, was a natural outcome of the research done on urea-formaldehyde products by Pollak [72], Ellis [73], Walter [74] and many others that reported several compounds with obvious uses like adhesives, moulding and impregnants for fabrics. In 1935 Henkel [75] patented the production of resins derived from the reaction of formaldehyde with melamine. Melamine-formaldehyde resins exhibit a distinct superiority over urea-base materials in thermal performance as well as moisture resistance. The commercialization of melamine resins started in 1939. They were used during World War II for the ignition systems of aircraft and tanks due to their high dielectric strength. They increase the wet-strength of paper so their use in the paper industry is extensive. The most public use of melamine resins is probably in the laminates such as "Formica" used in kitchens which are resistant to acids and boiling water, and form surfaces easy to clean.

## 2.3 Reactions Involved in the Production of Melamine Resins

Similar to urea, melamine reacts with formaldehyde over a wide pH range. The products are derived by methylolation of the amino groups to form additional products. The course of further reactions is dependant on the pH. Basic conditions promote further additional reactions with formaldehyde. Acid conditions lead to rapid condensation reaction. High pH is usually avoided in the synthesis of MeF resins, because of the competing Cannizzaro reaction. Lapina and Zharina (76) have shown a substantial loss of formaldehyde by formic acid formation above pH9 (table 2.2).

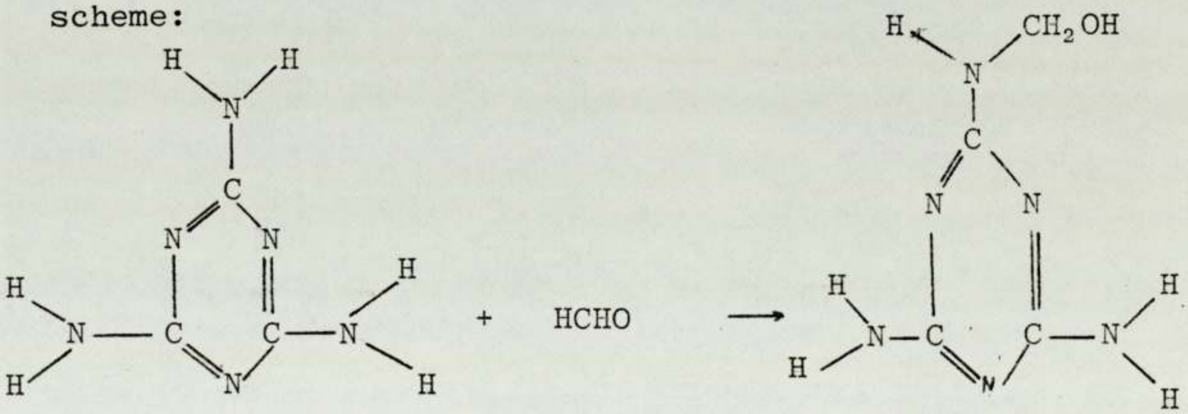
| pH during methylolation | HCHO lost by conversion into HCOOH | |
|---|---|---|
| | g | % of charge |
| 7-7.3 | 0.073 | 0.092 |
| 7.8-8.1 | 0.212 | 0.27 |
| 8.1-8.4 | 0.466 | 0.60 |
| 8.4-8.6 | 0.675 | 0.87 |
| 8.6-8.9 | 3.2 | 3.88 |
| 9.6-9.8 | 35.30 | 45.4 |

Table 2.2 Loss of formaldehyde by conversion into formic acid by the Cannizaro reaction, as a function of pH.

In melamine resins the etherification of the methylol derivatives is normally required to improve the solubility of the resin in organic solvents. Therefore, butylation is another reaction to be considered in parallel with the condensation reactions. During the manufacture of butylated formaldehyde melamine resins, an aqueous/alcoholic medium is used and the reactions take place simultaneously. However, for the sake of simplicity the three main reactions involved will be discussed separately.

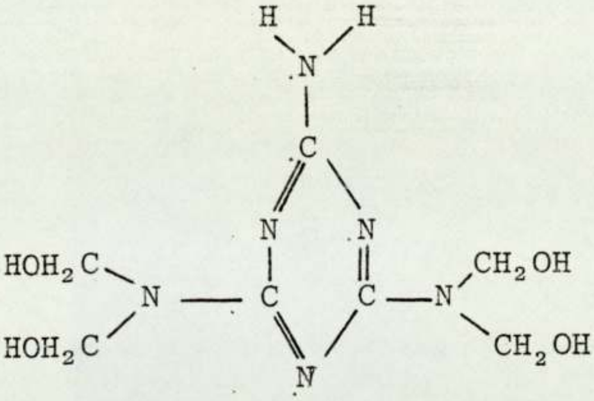
### 2.3.1 Methylolation Reaction

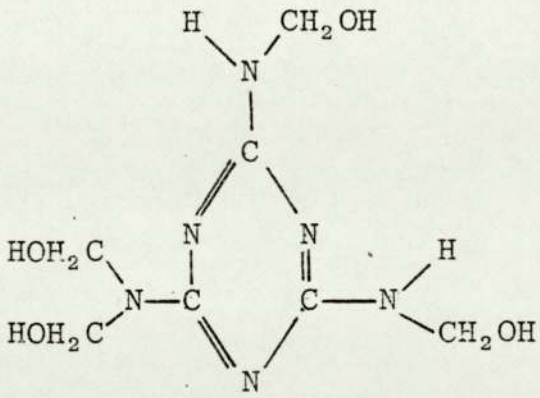
The methylolation reaction also designated by hydroxymethylation or addition reaction can be represented in a simplified way by the following reaction scheme:



Melamine Formaldehyde Monomethylol-melamine

Nine methylol melamines from mono to hexa-methylolmelamine are possible since the di tri and tetra methylol compounds each exist as two isomers. For example, the two possible isomers of tetramethylol melamine can be represented by,





Hodgins et alia [77] published a paper in 1941, where the chemical structure of methylol melamines and resins in general was discussed. Hexamethylolmelamine was found to be the most stable of the methylolmelamines, and a way to prepare and isolate it in the laboratory was explained. The trimethylol compound was also prepared but it was noticed that it was not stable and presented no definite melting point. It has been thought that a given molar ratio of formaldehyde to melamine F:M would produce the corresponding methylol melamine with a degree of substitution equal to the F:M ratio [78], i.e, a 3:1 ratio would yield trimethylolmelamine almost exclusively. On the contrary, Koeda [22-25] using paper chromatographic analysis proved that this idea was wrong Products up to hexamethylol melamine were formed even in the early stages of reaction in both dilute and concentrated reaction solutions. The reversibility of the reaction was proved by placing methylolated melamines in solution and noting the development of lower methylolated melamines by chromatography. Koeda also followed the acid-catalysed reaction of melamine with formaldehyde by paper chromatography (condensation). At pH = 5 and 70°C both methylolated and methylene bridges products were formed.

The latter were confirmed by paper chromatography by the appearance of bandlike images. These increased with time while the methylol melamines diminished in concentration. Koeda did not determine reaction rates but his work was a very important contribution for the general understanding of the chemistry of M:F resins. It also demonstrates the importance of a good and consistent method of analysis. Paper chromatography was used by other authors many years after the first paper by Koeda in 1954.

The first research on the kinetics of melamine chemistry was reported by Okano and Ogata in 1952 [79]. These authors studied the reaction of melamine with formaldehyde over a wide range of conditions. The consumption of formaldehyde was determined by the sulphite method. The total formaldehyde present as unreacted formaldehyde and as methylol was determined by iodometry. Thus the formaldehyde present as condensation bridges could be estimated by difference to establish the degree of condensation. In that way, Okano and Ogata were able not only to study the methylolation reaction but also the condensation reaction. The rate of reaction of melamine with formaldehyde to form methylol substitution products was determined at 35°C and 40°C in aqueous solution. The pH range was varied form 3 to 10.6. The authors found very little difference between the rates of formation of mono-di, and trimethylol melamines. In the reaction of formaldehyde with melamine the reaction mixture reached an equilibrium value of unreacted formaldehyde. A clear dependence on pH was shown to exist for the rate constant. A mechanism similar to the urea-formaldehyde reaction was proposed for methylolation under basic conditions,

$$\mathrm{Me} + \mathrm{OH^-} \rightleftharpoons \mathrm{Me^-} + \mathrm{H_2O} \qquad \text{(fast)}$$

$$\mathrm{Me^-} + \mathrm{HCHO} \rightleftharpoons \mathrm{Me\ CH_2O^-} \qquad \text{(slow)}$$

$$\mathrm{Me\ CH_2O^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{Me\ CH_2OH} + \mathrm{OH^-} \qquad \text{(fast)}$$

in which Me represents melamine.

Kveton and Hanousek [80] determined the rates of methylolation of melamine, monomethylolmelamine and dimethylolmelamine. They also found very little difference between the rates of methylolation. The temperature range used was form 40°C to 70°C and PH 7.7. They found no evidence of formation of tetra, penta and hexamethylolmelamines at low solution concentrations. This fact agrees with the findings of Okano and Ogato but they contradict the results of Koeda. The controversy was solved some years later, by Gordon et alia, and will be discussed further in the text.

Dixon et alia [81] determined the dissociation constants of melamine and some methylated methylol compounds by means of electronic titration and ultra-violet absorption spectrum. An increase in the number of methylol groups or in the degree of etherification tends to decrease the rate of polymerization. Therefore, the hydrogen ion concentration is a factor in controlling the rate of polymerization and consequently the basicity of the polymerizing melamine compounds affects the acidity of its solution influencing the rate of polymer formation. They found that the basic dissociation constants decreased from 1.1 x $10^{-9}$ for melamine to $10^{-12}$ for the hexamethylated hexamethylolmelamine. The value of the dissociation constants vary linearly with molecular weight of the melamine compounds. The results were obtained for methylol melamines having an average degree of formaldehyde substitution less than 3, $n < 3$. The same study was retaken by Tashiro and Shimura in 1974 [82] and results for higher degree of formaldehyde substitution were obtained.

One of the most complete works about the thermodynamic and kinetics of methylolation reaction was published in 1966 (83). The addition reaction between melamine and formaldehyde was separated from the subsequent condensation stage by suitable choice of concentration and temperature conditions. The temperature range selected was 25-55°C, the range of means degree of methylolation was $1 < R^1 < 3.7$ and pH was varied from 5.7 to 10.2. As a first approximation it was assumed that random reaction takes place between the formaldehyde molecules and the six reactive hydrogen atoms of melamine. The reaction scheme for the general case is shown in figure 2.1.

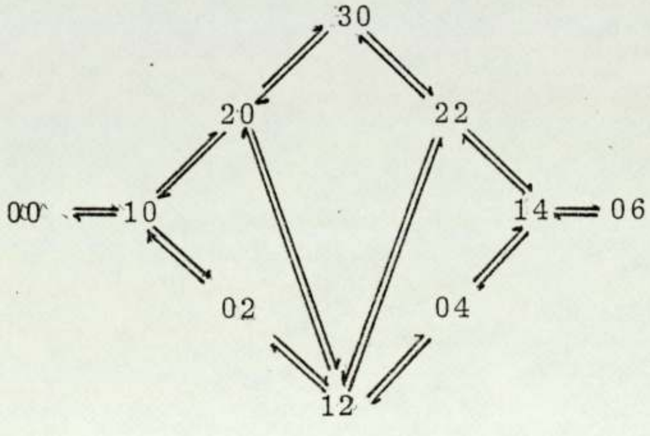
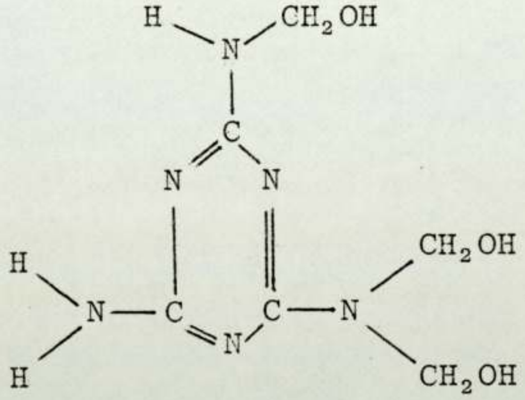


Fig 2.1 Reaction scheme for formation of methylol melamines [83]

The methylolmelamines are designated by the symbols i, j where i indicates the number of $CH_2OH$ groups on $NHCH_2OH$ groups, and j the number of $CH_2OH$ on $N(CH_2OH)_2$ groups in a given compound. For example 12 (i = 1, j = 2) describes the compound.



It was assumed that both methylolation and demethylolation reactions occur in a random manner with rate constants, $K_1$ and $K_2$. The mean degree of reaction of the distribution at any stage can be calculated from the fraction of amino hydrogen atoms which are methylolated.

In this way the authors were able to study the methylolation reaction as a whole instead of considering twelve different reversible reactions.

The rate of change of formaldehyde concentration is given by,

$$d[HCHO]/dt = -K_1[HCHO][-H] + K_2[-CH_2OH] \qquad (1)$$

where $K_1$ is the second order rate constant for methylolation and $K_2$ is the 1st order rate constant for demethylolation. At equilibrium,

$$K = \frac{K_2}{K_1} = \frac{[\mathrm{HCHO}]_e[-\mathrm{H}]_e}{[-\mathrm{CH_2OH}]_e} \qquad (2)$$

where K is the equilibrium constant for the demethylolation reaction. Let F be the molar ratio of reactants (moles HCHO/moles melamine), ae the equilibrium concentration of free formaldehyde, ao the initial concentration of free formaldehyde and K the equilibrium constant of the demethylolation reaction, equal to $K_2/K_1$.

Therefore,

$$[-\mathrm{CH_2OH}]_e = a_o - a_e$$

As melamine is hexafunctional $\frac{F}{6} = \frac{[\mathrm{HCHO}]_o}{[-\mathrm{H}]_o}$

$$[-\mathrm{H}]_o = \frac{6}{F} a_o$$

$$[-\mathrm{H}]_e = \frac{6}{F} a_o - (a_o - a_e)$$

Substitution in (2) gives

$$[(6/F) - 1] + a_e/a_o - K[(1/a_e) - (1/a_o)] = o \qquad (3)$$

the integration of eq (1) leads to

$$K_1 t = -\frac{1}{Y} \ln \left[\frac{(2a + g + K - Y)(2a_o + g + K + Y)}{(2a + g + K + Y)(2a_o + g + K - Y)}\right] \qquad (4)$$

where,

$$g = a_o[(6/F) - 1]$$

and,

$$Y = \sqrt{(g + K)^2 + 4Ka_o}$$

In order to conduct studies on equilibrium solutions and therefore use equation (3) it is necessary to be able to determine the free formaldehyde in solution. Gordon et alia used the modified iodine -sulphite method as used by de Jong and de Jong [84]. According to equation (3), if [(6/F) - 1] + ae/ao is plotted against $[(1/a_e) - (1/a_o)]$ a good straight line should be obtained. The slope of the straight line gives the value of K. That was in fact the case and a value of K equal to 0.237 mole/l was obtained. However, when the author calculated the individual K values (see table 2.2 ) a steady increase of K over a 1.65 fold range is observed as F increases 30-fold. This reflects deviations from randomness through substitution effects.

| F | K (mole/l) |
|---|---|
| 0.5 | 0.235 |
| 1.0 | 0.243 |
| 2.916 | 0.257 |
| 5.0 | 0.280 |
| 7.0 | 0.329 |
| 10.0 | 0.362 |
| 15.0 | 0.393 |

Table 2.3 - Equilibrium constant for pH demeythylolation as a function of F [83] Ph = 9.5, T = 45°C

In very much the same way the influence of temperature and pH on the value of K was studied. (Table 2.5 and 2.4).

| F | T (°C) | K (mole/1) |
|---|---|---|
| 3.0 | 25 | 0.192 |
| 3.0 | 30 | 0.222 |
| 3.0 | 35 | 0.248 |
| 2.916 | 45 | 0.257 |
| 3.0 | 55 | 0.324 |
| 7.0 | 25 | 0.210 |
| 7.0 | 30 | 0.226 |
| 7.0 | 35 | 0.259 |
| 7.0 | 45 | 0.329 |
| 7.0 | 55 | 0.327 |

Table 2.4 - Equilibrium constant for demethylolation as a function of temperature [83] pH = 9.5.

Using a Van't Hoff plot (ln K as a function of 1/T ) the heats of reaction of -2.95 and -2.8 ± 0.3 Kcal/mole were found for F = 30 and 7.0 respectively. From eq 5 and 6 $\Delta G^\circ$ = 850 cal/mole and $\Delta S^\circ$ = 6.5 cal/mole/deg were determined.

$$\Delta G^\circ = KT \ln K \qquad (5)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \qquad (6)$$

These thermodynamic functions refer to average values over the various positions on various substituted melamines.

| pH | K mole/l |
|---|---|
| 5.7 | 0.193 |
| 6.6 | 0.217 |
| 7.5 | 0.257 |
| 8.6 | 0.273 |
| 9.5 | 0.257 |
| 10.2 | 0.281 |

Table 2.5 - Equilibrium constant for demethylolation as a function of pH [83] F = 3; T = 45°C

It was found that the equilibrium constant is reasonably independent of the pH.

Having obtained the experimental values for equilibrium, Gordon et alia calculated the rate constant of methylolation for different conditions. This was done by using equation (4).

| F | $K_1 \times 10^4$ l/mole sec |
|---|---|
| .5 | 6.4 |
| 1.0 | 7.67 |
| 2.196 | 4.58 |
| 5.0 | 3.75 |
| 7.0 | 3.33 |
| 10.0 | 2.45 |
| 15.0 | 1.95 |

Table 2.6 - Methylolation rate constant as a function of F [83]

A variation of 30-fold in F values causes a variation of four fold in the kinetic constant. This proves that the assumption of randomness of the reaction gives at best a semiquantitative picture of the system. It is apparent as methylolation proceeds, it becomes increasingly more difficult to replace amino hydrogen atoms by methylol groups.

By studying the variations of the methylolation rate constants with temperature the activation energies for methylolation and demethylolation were found to be respectively $\Delta E_1$ (methylolation) = 23.6 k cal/mole and $\Delta E_2$ (demethylolation) = 26.7 k cal/mole.

A marked dependence of $K_1$ on the pH of solution was also found.

| F | Temperature (°C) | $K_1 \times 10^4$ |
|---|---|---|
| 3.0 | 25 | .25 |
| 3.0 | 30 | .64 |
| 3.0 | 35 | 2.30 |
| 2.916 | 45 | 6.25 |
| 3.0 | 55 | 7.10 |
| 7.0 | 25 | .22 |
| 7.0 | 30 | .37 |
| 7.0 | 35 | 2.30 |
| 7.0 | 45 | 4.30 |
| 7.0 | 55 | 6.80 |

Table 2.7 - Methylolation rate constant as a function of temperature pH = 9.5 [83]

This paper was the most detailed study in the 60's of the addition reaction between melamine and formaldehyde. A considerable amount of thermodynamic and kinetic data was published and certainly it contributed to a better understanding of the initial reaction of the manufacture of melamine resins. This information is not directly usable for the industrial production of melamine resins since the medium used in the manufacture is aqueous/alcoholic whereas the data refers to dilute aqueous solutions.

The influence of the medium in the reactions was studied by Schedlbauer [89] much later and this work is described in section 2.4.

The work on the additon reaction was continued by the same authors [85] using a different approach. By using Koedas' method it was shown that an equilibrium exists between melamine, formaldehyde and methylolmelamines and that these equilibrium mixtures can be separated by paper chromatography. The nine possible methylol compounds have been allocated to the chromatographic spots and by use of $C_{14}$ - labelled formaldehyde [86] the relative proportion of each methylol compound, in the various equilibrium mixtures studied, were determined. The experimental distribution was compared with that calculated for a random reaction and minor deviations were explained in terms of a more general distribution containing two further parameters arising from chemical substitution effect [87]. The random reaction scheme can be represented by the Bernoulli distribution.

$$n_r = C_r \, p^r \, (1 - p)^{6 - r} \qquad (7)$$

where:

$n_r$ represents the fraction of melamine nuclei bearing r methylol groups

p represents the overall fraction of amino hydrogen atoms substituted by methylol groups

$C_r$ combinational factors

The existence of isomers requires a way to distinguish between secondary amino groups $NH(CH_2OH)$ and tertiary amino groups $N(CH_2OH)_2$. The distribution can be written in more detail denoting r = i + j, by equation (8).

$$n_{ij} = c_{ij} \, p^{i + j} \, (i - p)^{6 - i - j} \qquad (8)$$

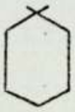
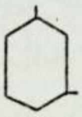
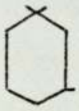
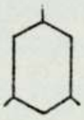
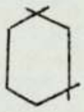
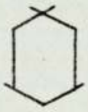
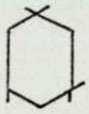
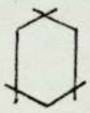
where:

i represents the number of methylol groups belonging to secondary amino groups ($RNHCH_2OH$)

j represents the number of methylol groups belonging to tertiary amino groups ($R(CH_2OH)_2$)

and $c_{ij}$ is given in table 2.7

R = 6p - mean degree of substitution

| Methylol Compound |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| i | 0 | 1 | 0 | 2 | 1 | 3 | 0 | 2 | 1 | 0 |
| j | 0 | 0 | 2 | 0 | 2 | 0 | 4 | 2 | 4 | 6 |
| $c_{ij}$ | 1 | 6 | 3 | 12 | 12 | 8 | 3 | 12 | 6 | 1 |

⬡ melamine residue    ı methylol group

Table 2.8 - Combinational factors [86]

Using equation (8) the experimental and calculated values were compared and some deviations occur especially with compounds having $N(CH_2OH)_2$ groups . It was found that these groups were formed in smaller proportions than the random theory predicted. That revealed that secondary amino hydrogen is less reactive than primary ones. In order to account for the loss of reactivity of hydrogen atoms a new general distribution containing two further parameter x and y was considered.

$$n_{ij} = N c_{ij} x^{(i+j)^2} y^{j/2} q^{i+j} (1-q)^{6-i-j} \qquad (9)$$

N - normaliser

q - replaces conversion parameter p (if $x = y = 1$ $p = q$)

x - parameter for general substitution effect

y - local substitution effect

The parameter x is a measure of a general substitution effect, i.e, one extending over the melamine nucleus as a whole; a linear activation effect results from $x > 1$ and a deactivation from $x < 1$. Gordon and Scantlebury [87] and Bjerrum [88] demonstrated that the free energy of forming a melamine formaldehyde bond should vary linearly with the number of methylol already carried by the melamine nucleus.

The parameter y accounts for the observed deactivation ($y > 1$) of any hydrogen atom by virtue of the prior substitution of the other hydrogen on the same amino group by a methylol group. The optimum values of these parameters have been derived $x = 1.125$ and $y = 0.5$. In a later paper Aldersley [55] reinvestigated in detail the model and by computer simulation of a kinetic model containing eleven ordinary differential equations found x = 1.011. That value reduces the effect so much further, that it was found more sensible to fit the data assuming the general effect absent (x = 1). In fitting any data, the two values of x and y are correlated so that a change in the value of one can to some extent be compensated by changing the other. The reduction of x = 1 lead to an increase in the optimum value of y, found equal to 0.61 ± 0.02.

Tomita [48] investigated the additon reaction between melamine and formaldehyde by direct observation with NMR spectroscopy and high speed liquid chromatography. The use of these quantitative methods permitted the estimation of equilibrium constants and rate constants for the individual reversible reactions in aqueous solution at pH = 9.0 and temperature equal to 28,38 and 48°C.

All nine methylolmelamines were detected and the isomers were successfully separated by high speed chromatography. For the equilibrium calculations it was noticed that four hours at 48°C, 30 hours at 38°C and 120 hours at 28°C were necessary for the reaction to reach equilibrium. The temperature dependence of each equilibrium constant was calculated from a Van't Hoff plot, giving analogous heats of a mild exothermically of -3 to -3.5 K cal/mole for each methylolation, value in agreement with the one reported earlier by Gordon et alia [83].

The data also indicated that the methylolation of melamine nuclei becomes increasingly difficult with an increase in the mean degree of addition.

Schedlbauer[89] studied the formation and composition of melamine resins under conditions similar to practical production. The addition of formaldehyde was studied both in water solution and with paraformaldehyde in butanol solution. The final products were characterised for total formaldehyde, free formaldehyde and content of butoxy groups. It was observed that at 90°C and pH = 6.6 equilibrium in aqueous solution of the methylol species was reached in less than half an hour for any formaldehyde/melamine ratio. That was not so for the addition in butanol solution. In this case, equilibrium took 2 to 3 hours to be established, but the amount of formaldehyde reacted exceeded the corresponding amount for aqueous solutions. This behaviour can be explained by the constant reaction of the methylol groups with butanol (butylation reaction).

Possibly the most detailed study on the mechanisms of the methylolation and condensation reactions is attributed to Sato. The methylolation of melamine and urea with formaldehyde was first studied thermodynamically in aqueous solution [90]. The entropy, enthalpy and free energy of activation for the early stages of reaction, i.e, the formation of monomethylol derivative and also the thermodynamical properties in connection with the functionalities were determined. The results found agree with the ones calculated by Gordon et alia. Moreover, the solvent effect of dimethylsulfoxide in the methylolation reaction was investigated [90, 91]. It was clear when a small amount of dimethylsulfoxide (DMSO) was added to an aqueous solution the rate constants decreased. This effect was explained by the polar nature of DMSO. It dissolves a certain amount of melamine, suggesting a facility of solvation between these substances and analogously one between DMSO and formaldehyde. Such solvation hinders the effective collision between the active centers of the reactants and consequently the rate constant decreases. However, DMSO was found to be a good solvent because of its ability to dissolve condensation products.

One of the problems that made kinetic studies of resins difficult was the insolubility of condensation products in aqueous solutions. The solutions would become turbid and the reaction medium heterogeneous. Therefore, the choice of an adequate solvent that does not interfere with the analytical tests of the products (sulfite and iodometric methods - see appendix 2) was a condition to permit studies on the late stages of methylolation and condensation reactions of formaldehyde resins.

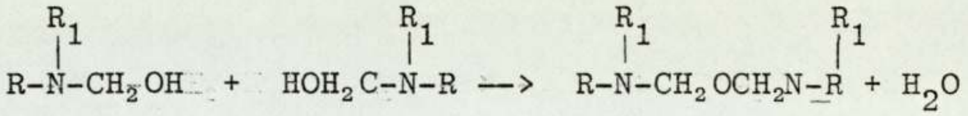
In later papers Sato et alia [92, 93, 94] investigated the early stages of monomethylolmelamine formation in different pH regions. Dilute aqueous solutions were used and the pH was varied by addition of different properties of hydrocloric acid.

The methylolation reaction rate, in mild acid conditions pH 3 to 8, was found to be dependent on the concentration of melamine molecule MH and its conjugate acid $MH_2^+$. This study completed the mechanism proposed earlier by Okano et alia [79] and the methylolation rate constant was found to be the sum of several contribution reactions of chemical species that owe their existence to the pH conditions of the solution under study. Similar studies were done by Tashiro et alia [95] for a methylated product of melamine and the reaction mechanism proposed was similar to the one advanced by Sato.

The studies by Sato focussed on the influence of the pH of the medium on the reaction rates and the interrelation of acid-base equilibrium in the mechanism of the reactions. The mechanisms proposed are complex and theoretically elaborated. The applicability of these studies is however questionable since the reaction conditions used are very distant from the conditions used in industry. The complexity of the rate equations for the formation of a single methylol compound showed us the need of a global approach for the modelling of the reactions involved in the manufacture of butylated melamine formaldehyde resins. By a global approach is meant an average characterisation of the reaction mixtures by parameters like degree of methylolation instead of the exact concentration of all the chemical species in the reaction vessel.

### 2.3.2 Condensation Reaction

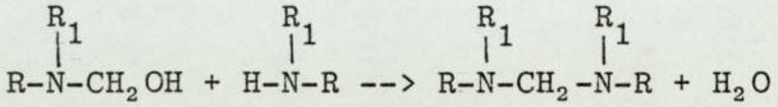
After the addition stage of the reaction, with, the formation of methylol melamines, these water insoluble products react further, yielding condensation products (polymers). In the simplest cases, two methylol groups lead to a methylene ether linkage and a methylol and amino group give a methylene bridge. The reaction can be represented by the following equations:



$$R-\overset{R_1}{\overset{|}{N}}-CH_2OH + HOH_2C-\overset{R_1}{\overset{|}{N}}-R \longrightarrow R-\overset{R_1}{\overset{|}{N}}-CH_2OCH_2N-\overset{R_1}{\overset{|}{R}} + H_2O \qquad (10)$$

(methylol melamine) (methylene ether bridge)

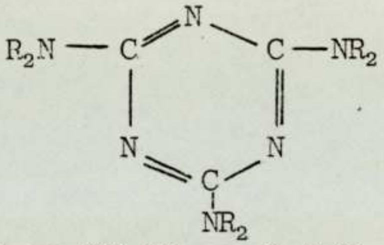
or:



$$R-\overset{R_1}{\overset{|}{N}}-CH_2OH + H-\overset{R_1}{\overset{|}{N}}-R \longrightarrow R-\overset{R_1}{\overset{|}{N}}-CH_2-\overset{R_1}{\overset{|}{N}}-R + H_2O \qquad (11)$$

methylene bridge

where R represents



$R_1$ and $R_2$ represent H or $CH_2OH$ or $C_4H_9O$

In this way, polymers with variable molecular weight are formed. Kitagawa [100] studied the condensation reactions of melamine resins and showed that reaction (11) is a second order reaction. In the case in which 3 moles of formaldehyde to 1 mole of melamine was used reaction (1) seems to be the main reaction. However when higher molar ratios were used methylene ether bridges were also present in the condensate product [101]. Wohnsiedler [104-105] found that the self condensation of melamine resins takes place mainly by the formation of methylene linkages. However he refers to the possible formation of methylene-ether bridges in alkaline medium, and two other type of hypothetical bonds:

1) A structure arising from reaction of two methylol groups on different molecules to yields a modified

type of methylene bridge containing a free methylol group.

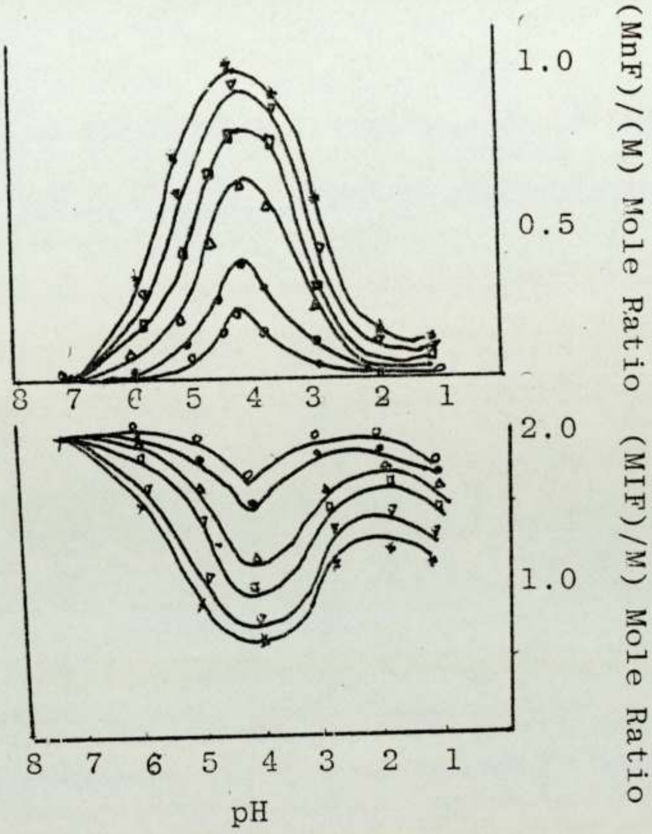
2) A structure arising from a ring closure reaction involving two methylol groups on the same nitrogen atom.

Some other possible structures are referred to in the literature [102-103] but there is no proof they occur in the manufacture of formaldehyde melamine resins.

### 2.3.2.1 Formation of the Methylene Linkage

Okano and Ogato [79] were among those to investigate the kinetics of the condensation of melamine with formaldehyde in aqueous solution at 35, 40 and 70°C by employing both iodometric and sulphite methods for the calculation of the reacted formaldehyde. At low temperatures no evidence of condensation product formation was found. However at 70°C some condensation products were formed in neutral and acidic media. The condensation rate was expressed as second order to melamine concentration and first order to formaldehyde concentration. This rate equation was found to apply for the early stages of reaction (up to 35% of formaldehyde reacted). As the reaction proceeds the reactivity falls rapidly because of the production of sterically hindered amino groups in the condensate.

The condensation reaction rate is known to be dependent on the pH of the solution, in which it takes place. In the curing of methylolmelamine an acid catalyst is usually added first, prior to the cure because the condensation rate increases remarkably upon the addition of a small amount of an acid [106]. The condensation reaction of di, tri and hexamethylolamines was investigated by Sato, in the range of pH 8-1. An aqueous-dimethysulfonide (DMSO) solution (ca 1:2, vol ratio) was used as the solvent, because it is a good solvent for melamine, methylolmelamine and the condensate, and neither the iodometric nor the sulphite method are affected by the presence of a small amount of DMSO. Moreover, methylolmelamines were found to decompose hardly at all into lower methylolmelamines in DMSO or even in an aqueous-DMSO solution (1:2, vol ratio); consequently, the condensation mechanism of a methylolmelamine with a different number of methylol groups could be studied by the use of an aqueous-DMSO solution, even in the latter stage of condensation [107-108]. A typical result of this study is shown in fig 2.2, for the case of a compound with a composition near di-methylolmelamine.



o: 0.25 ●: 0.5 Δ: 1.0 □: 1.5

∇: 2.5 *: 3.5 Reaction Time (hr)

Initial Concentration (M 1.98 F) = 0.0634 (mol/l)

(MnF): Methylene linkage

(M): Melamine

(MIF): Methylol Group Concentration

Fig 2.2 - Condensation rate vs pH and decrease rate of methylol group concentration $v_S$ pH. (108)

The pH of the solution was varied by addition of different amounts of hydrochloric acid. Therefore, the initial pH of the solution was a function of [Hcl]/[Methylol] molar ratio. Samples were taken at appropriate intervals of time and were analysed by the iodometric and sulphite methods after neutralization. The pH values were measured by means of a glass electrode pH meter.

It is very clear that the condensation rate of M 1.98 F, approximately dimethylolmelamine, shows a maximum value in each curve at [Hcl]/[M] = 0.5 (molar ratio) in the early stage of reaction. The maximum was found to shift toward smaller [Hcl]/[M] values as the condensation proceeds. The above fact is explained by the fact that the condensate is less basic than the starting methylolmelamine. Similar results were obtained for the condensation reaction of trimethylolmelamine and hexamethylolmelamine. High methylolmelamines like hexamethylolmelamine show a maximum reaction rate initially at [Hcl]/[M] = 1.0, but that maximum shifts toward a smaller ratios approaching that of a low methylolmelamine with an elevation in temperature. Based on these results Sato proposed a mechanism for the early stage of condensation. The condensation rate equation was written as a sum of three terms:

$$R_c = K_1[MCH_2OH]^2\text{(molecular form, molecular form)} +$$
$$K_2[MCH_2OH][\overset{+}{H}MCH_2OH]\text{(molecular form, conjugate acid)} +$$
$$K_3[\overset{+}{H}MCH_2OH]^2\text{(conjugate acid, conjugate acid)}$$

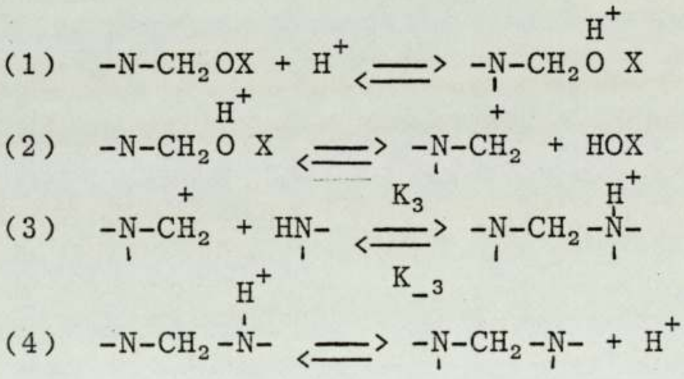
where $K_1$, $K_2$ and $K_3$ are the respective rate constants of the elementary reactions. The presence of the conjugate acid of a methylolmelamine is dependent on the pH of the solution and the equilibrium in eq (12).

$$MCH_2OH + H_3O^+ \overset{K}{\rightleftharpoons} \overset{+}{H}MCH_2OH + H_2O \qquad (12)$$

$$K = \frac{[\overset{+}{H}MCH_2OH]}{[MCH_2OH][H_3O^+]} \qquad (13)$$

The structure of the conjugate acid has been demonstated by Dixon et al [81] on the basis of an ultraviolet absorption spectra. In a later paper [109] Sato et alia proved that at pH 2-7 the main reaction at the early stage of the condensation is the reaction between the methylol melamine molecule and the conjugate acid. For pH < 2 the main condensation would be the reaction between the conjugate acid themselves.

Berge [99] also studied the kinetics of the condensation reaction and proposed the following mechanism:



(14)

$$
\begin{aligned}
&(1)\quad -N-CH_2OX + H^+ \rightleftharpoons -\underset{|}{N}-CH_2\overset{H^+}{O}\,X\\
&(2)\quad -N-CH_2\overset{H^+}{O}\,X \rightleftharpoons -\underset{|}{N}-\overset{+}{C}H_2 + HOX\\
&(3)\quad -\underset{|}{N}-\overset{+}{C}H_2 + H\underset{|}{N}- \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} -\underset{|}{N}-CH_2-\underset{|}{\overset{H^+}{N}}-\\
&(4)\quad -N-CH_2-\overset{H^+}{N}- \rightleftharpoons -\underset{|}{N}-CH_2-\underset{|}{N}- + H^+
\end{aligned}
$$

A methylol group (X = H) or an alkoxymethyl group (X = alkyl) is activated with the formation of a carbonium ion. The carbonium ion reacts in the rate determining step with an amino group leading to the formation of a methylene bond. By assuming this mechanism, the following rate equation for condensation was arrived at:

$$r_c = K_c\ [-CH_2OH][-NH] \qquad (15)$$

In which $r_c$ is the reaction rate of condensation (formation of methylene bridges) and $K_c$ is the condensation rate constant dependent on the pH of the solution and several acid dissociation constants. An experimental curve for the initial rate of condensation of trimethylolmelamine with melamine is shown in fig 2.3, [110].

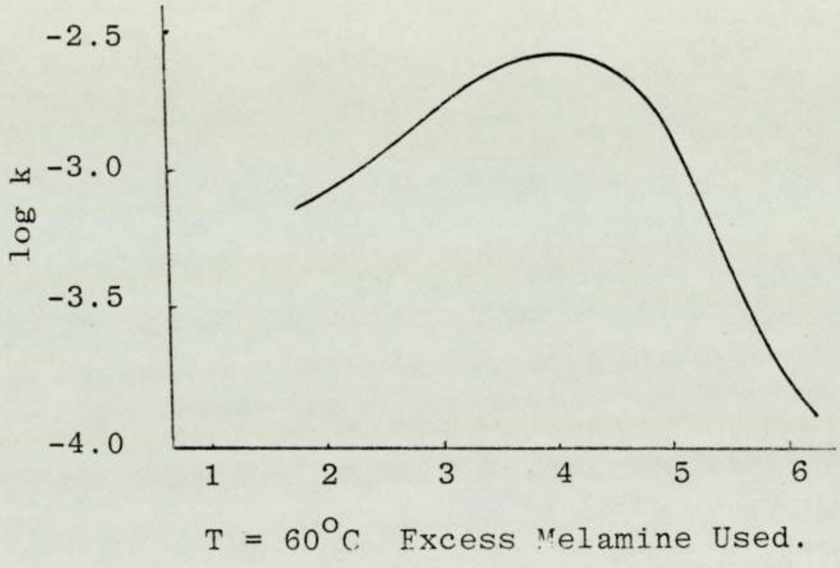


Fig 2.3 - Condensation of Trimethylolmelamine vs pH [110].

The reaction path given by Berge is included in the mechanism of reaction discussed by Sato. Sato claims, however, that the ring protonated methylol compound is most unlikely to be the dominating reactive specie, while Berge considers that the acid catalysed activation takes place by addition of a proton to the side chain. A discussion about this point is outside the scope of this work. It is clear, however, that the condensation reaction is a second order reaction and that the acid is a catalyst for this reaction.

### 2.3.22 Formation of Methylene Ether Bridges

Several authors have reported in the literature the existence of methylene ether bonds in the structure of the amino resins, and the reaction scheme for its formation is represented by equation (10). There is no published work on the mechanism of this reaction and the reason for this is probably the lack of reliable analytical and/or instrumental methods of anlysis to monitor the reaction for butylated formaldehyde melamine resins. In the last ten years there was a noticeable advance in the analytical methods of analysis and some research was done to determine quantitavely the dimethylene ether bridges in the resins structure.

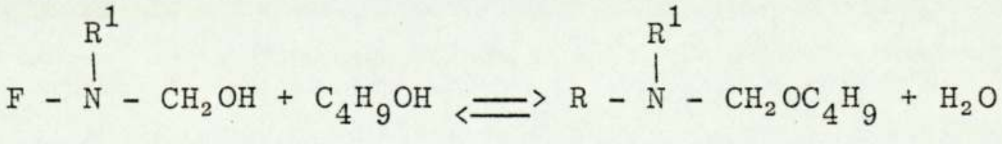
Berge [99] reported a chemical method of analysis in which the determination of dimethylene ether groups is possible in alkaline solution. He claims that methylol groups, butoxy groups and dimethylene ether bridges may be calculated by an appropriate choice of reaction conditions. He applied it to an alkylated melamine formaldehyde resin and the functional groups were calculated.

Chiavarini et alia [51] published a method of composite characterization of melamine formaldehyde condensate by combining NMR spectroscopy and chemical analysis. By this method it was possible to determine the content of methylol, methylene and methylene ether bridges and of non substituted, monosubstituted and disubstituted amino groups. They applied it to study the structural changes which occur during the two step condensation of urea-formaldehyde resins. In mildly acid conditions the condensation takes place through the formation of methylene linkages (= N-$CH_2$-N =) and in alkaline medium the reaction was found to proceed via the formation of methylene ether bridges = N - $CH_2OCH_2$ - N =. The same result was obtained by Kambanis and Vasishth who found the dimethylene ether linkage stable in alkaline medium whereas in acid conditions the dimethylene ether bridges cleave and the methylene bridges are stable [111].

### 2.3.3 The Etherification of the Methylolmelamines with n-Butanol-Butylation

In the manufacture of melamine formaldehyde resins the reaction takes place in alcoholic medium to promote etherification of the methylolmelamine formed by methylolation in the first stage of reaction.

This reaction takes place in mild acid conditions in parallel with the condensation reaction (see section 3.1.2). Very little information about this reaction is available in the literature. Some papers were found about the etherification of melamine-formaldehyde resins with sec-butanol [112,113], but only one about the butylation with n-butanol [89], the reactant that is used in the resins under study in this work. The butylation reaction can be represented by the following reaction scheme:



$$F - \overset{R^1}{\overset{|}{N}} - CH_2OH + C_4H_9OH \Longleftrightarrow R - \overset{R^1}{\overset{|}{N}} - CH_2OC_4H_9 + H_2O$$

(16)

where R represents the basic melamine ring and $R^1$ hydrogen or methylol group. Schedlbauer [89] investigated the butylation reaction under conditions similar to industrial production. Paraformaldehyde in butanol solution was the initial medium selected. He found that the butanol concentration does not influence the rate of reaction, i.e the butylation reaction is pseudomonomolecular. The rate equation can, therefore, be expressed as a function of methylol concentration groups only. The butylation was started after one hour of reaction time, to allow the methylolation reaction to reach equilibrium, by addition of an acid. The temperature was then raised to boiling and the reaction water was removed by azeotropic distillation with butanol. The temperature variation in the reaction vessel was from 98°C to 120°C. Different acids were tried as starters of the butylation reaction. It was found that the stronger the acid is, i.e, the lower the pH value is made, the further the butylation goes. That effect is shown in fig 2.4.

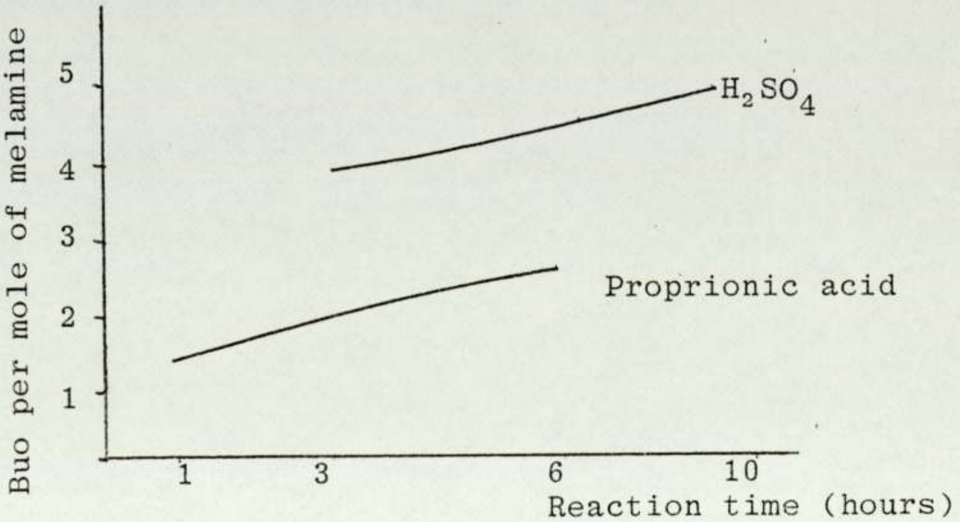


Fig 2.4 - Etherification of Melamine Resins vs Reaction Time T = 120°C 6.5 moles Butanol/mole of Methylolmelamine [89]

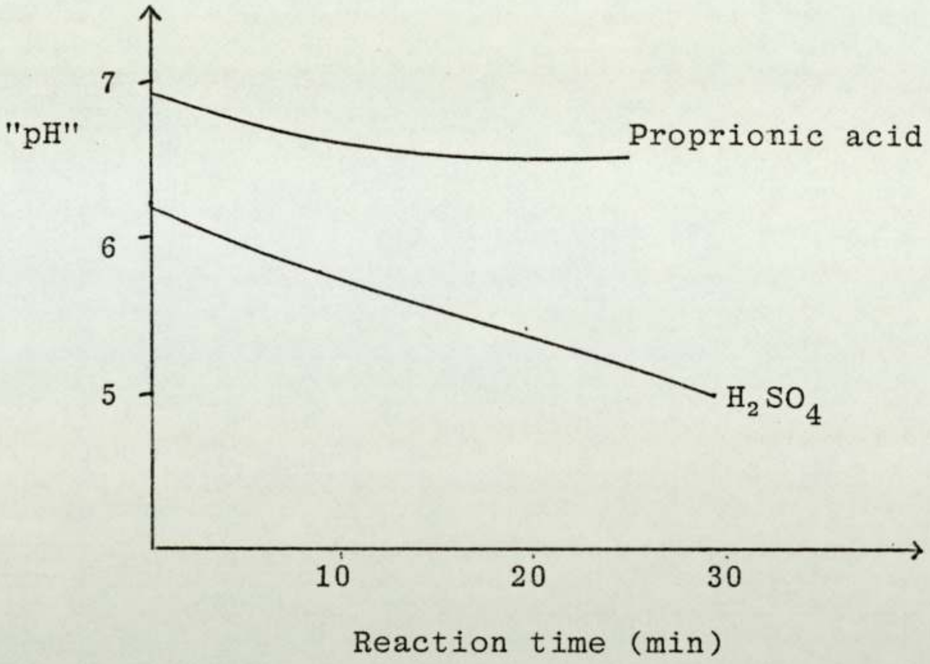


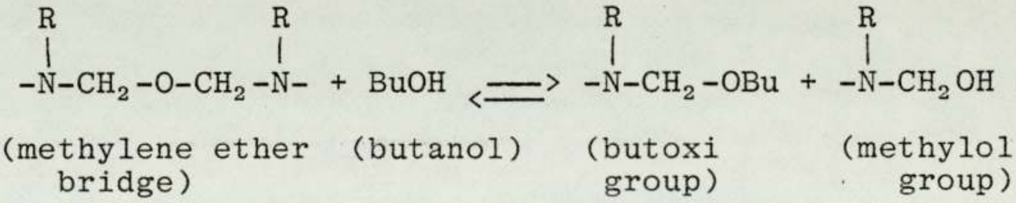
Fig 2.5 - pH vs Reaction time

The butylation was shown to be dependent on the pH of the media. The influence of the acid catalyst anion was not fully explained, but viscosity measurements showed that when acetic acid or propionic acid are used the resins formed have a noticeable lower viscosity than when phosphoric acid or sulphuric acid are used as a catalyst. It was pointed out that when aqueous solutions of formaldehyde (formalin) are used as reactant the reaction medium becomes a mixed aqueous/alcoholic solution and the resins produced are more viscous than the ones resulting from an exclusive alcoholic media. Than can be explained by the reversibility of equation (16).
High water content promotes the inverse reaction of butylation, and the methylol melamines tend to react in this case via the formation of methylene bridge formation which is irreversible. Thus, the water content of the solution when acidification takes place, is an important factor in the balance between the butylation reaction

and the condensation reaction.

By using chemical analytical methods Schedlbauer calculated the composition of synthesized resin and analysed its changes during the course of reaction. His results are shown in table 2.9.

The interesting point about table 2.9 is the behaviour of the resin for formaldehyde/melamine ratio equal to 6. At 3 hour of reaction the number of bridges originated by condensation is higher than for 13 hours of reaction. This means that initially methylene ether bridges are formed, that react with butanol later to yields methylol groups and butanol. Therefore, it is clear that for the reaction conditions in the industrial manufacture of butylated melamine formaldehyde resins the splitting of methylene ether bridges in acid medium has to be taken into consideration. This reaction can be represented by equation (17).

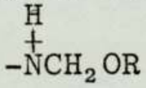
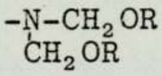


$$-\overset{\overset{R}{|}}{N}-CH_2-O-CH_2-\overset{\overset{R}{|}}{N}- + BuOH \rightleftarrows -\overset{\overset{R}{|}}{N}-CH_2-OBu + -\overset{\overset{R}{|}}{N}-CH_2OH \quad (17)$$

|  | Initial Charge Formaldehyde/Melamine Ratio |  |  |
|---|---|---|---|
|  | 4.7 Mole | 5.3 Mole | 6 Mole |
| After 3 hours of etherification |  |  |  |
| Formaldehyde added | 3.76 = 80% |  | 4.47 = 74.5% |
| There of etherified (butoxi) | 2.24 = 60% |  | 2.76 = 62% |
| Bridges per Melamine unit | .70 mole |  | .57 mole |
| Methylol groups | .82 mole |  | 1.14 mole |
| After 13 hours etherification |  |  |  |
| Formaldehyde added | 4.14 = 88% | 4.68 = 88% | 5.30 = 89% |
| There of etherified | 2.93 = 76% | 3.56 = 76% | 4.25 = 80% |
| Bridges per Melamine Unit | 1.07 mole | .88 mole | .11 mole |
| Methylol groups | 0.14 mole | .24 mole | .94 mole |

Table 2.9 Molecular structure of different melamine resins (referred to 1 mole of melamine) [89]. Butanol/melamine ratio = 6.5)

## 2.3.4 Decompositon of Ethers - Demethylolation, Debutylation and Cleavage of Methylene Ether Bridges

Berge et alia investigated the decomposition of trimethylolmelamine (TMM), methylated trimethylol melamine (TMM - Me), hexamethylol melamine (HMM) and hexamethoxymethyl melamine (HMM - Me) in alkaline and acid conditions [96, 97]. These studies called attention to an important point that has been often disregarded in the literature The stability of ether groups towards hydrolysis in alkaline conditions depends on whether or not there is a free H-atom on the nitrogen atom to which the alkoxy methyl group is attached. For example, a primary ether group like  $-\overset{H}{N}CH_2OR$ behaves differently from a secondary ether group like  $-\underset{CH_2OR}{N}-CH_2OR$ under alkaline and acid hydrolysis.

This research work has to do with the chemistry of the manufacture of melamine resins in three different ways:

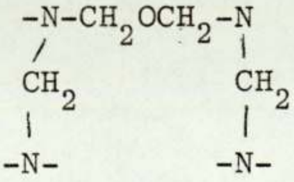
1. Demethylolation - methylol melamines decompose into melamine or lower methylol-melamines and formaldehyde. Under alkaline conditions, this reaction was found to be first order relatively to the methylol group concentration. The initial rate of decomposition of TMM was found to be higher than that of HMM which shows that a primary methylol group decomposes at a higher rate than a secondary methylol group. The rate constant for the decomposition of HMM increases markedly with the conversion as would be expected since the relative content of primary methylol groups increases during the reaction. Therefore, the decomposition rates of TMM and HMM tend to be equal at high

degrees of conversion.

2. The reverse reaction of butylation debutylation in which an alkoxy group, in the case of butylated resins, a butoxi group, decomposes to give an alcohol (butanol) and a methylol group.

   Berge et alia [96] used TMM-Me and HMM-He to study the mechanism of the reaction under alkaline conditions. It was found that secondary ether groups, like in HMM-Me, do not hydrolyse in alkaline solutions. The hydrolysis of primary ether groups takes place at a slow rate. It was found that the decomposition rate of TMM-Me is about 1/400 of the TMM decomposition rate. Therefore, it can be concluded that under alkaline conditions the reversible reaction of etherification is not significant.

3. Decomposition of dimethylene ether bridges $-\overset{R}{\overset{|}{N}}-CH_2OCH_2-\overset{R}{\overset{|}{N}}-$ (sec 2.3.2.2.), is expected to occur slowly under alkaline conditions like with TMM-Me if there exists an active H atom at one or both of the nitrogen atoms, i.e, if R = H. However, dimethylene ether groups which are stable towards alkali may also be present since no hydrogen atom is attached to the nitrogen atom. An example of this is the following structure.



$$\begin{array}{ccc} -N-CH_2OCH_2-N & & \\ / \qquad\qquad\quad | & & \\ CH_2 \qquad\quad CH_2 & & \\ | \qquad\qquad\quad | & & \\ -N- \qquad\quad -N- & & \end{array}$$

Under acidic conditions the decomposition of alkoxy groups and dimethylene ether bridges is much faster than the subsequent decomposition of methylol groups.

The manufacture of melamine resins can be divided into two stages (see section 3.1.2 ). First stage under mild alkaline conditions and second stage under acid conditions. The study of the stability of ethers by Berge indicates that in the first stage of the manufacture of butylated melamine resins, butoxy groups and methylene ether bridges are going to be present together with a mixture of methylol melamines. In the second stage the dimethylene ether bridges are decomposed together with some butoxy groups. However, due to the increase of methylol groups the butylation reaction proceeds faster and the effect of the decomposition of butoxy groups is overshadowed by a faster formation of the same group by butylation. The condensation via the methylene bridge formation is also promoted due to the increase of methylol groups concentration and the stability of methylene bonds in acidic medium. The condensation reaction can be assumed to be irreversible in acid conditions.

## 2.4 Instrumental Analysis

In recent years analysis and characterisation of the chemical structure and molecular species of the formaldehyde resins have progressed significantly by means of instrumental analysis involving gas chromatography (G.c), pyrolysis gas chromatography (PGC), high performance liquid chromatography (HPLC) with various modes such as absorption, partition and specially site exclusion (Gel Permeation Chromatography - GPC), gas chromatography, mass spectrometry, infrared spectrometry (IR), proton and carbon-13 nuclear magnetic resonance spectrometry ($^1$H-NMR and $^{13}$C-NMR) and so on.

The first instrumental analaysis was applied as long ago as 1954 by Koeda. He published a series of papers [22-25] on the condensation products of melamine with formaldehyde. Paper chromatography was used for the separation of all the methylol melamines (mono to hexa) in the addition stage. Later, the same technique was used by Gordon [26] to test a reaction model for the methylolation stage.

Column chromatography was applied to analyse mononucleur methylol melamines (monomer) present in the formaldehyde resins using a dextran gel (Sephadex LH-20) column and DMF as the mobile phase [27-29].

Numerous chemical and instrumental techniques have been described for the qualitative and quantitative analysis of melamine resins before 1970, [30-33], but it was in the seventies that a major step forward in the consistent study of the structure of melamine condensates was achieved by the use of Gel permeation chromatography (GPC).

The fact that molecules could be separated by virtue of their size was noticed in experiments on electrophoretic and ion-exchange separations over thirty years ago. However, GPC was recognised to be useful in the analysis of melamine resins much later. It was used for the fractionation of polymers and also for the separation of mixtures of compounds of lower molecular weights. Compared with traditional methods such as precipitation and turbidimetry it shows a saving on both time and labour, and the results obtained are more reliable.

One of the first works published on GPC for the determination of molecular weight distributions of resins produced by reaction of formaldehyde with phenols, melamine or urea, was by Aldersley et alia in 1969 [34]. By that time some literature had appeared on the use of $^{1}$H-NMR and GPC for the characterisation of monomeric and polymeric etherified methylolated melamine [35, 36]. In 1970, a paper by Anderson et alia was published where a series of monomeric etherified melamines were prepared and characterised by $^{1}$H-NMR and GPC. GPC analysis permits a rapid and accurate determination of the monomer and polymer content of the products, whereas proton magnetic resonance spectroscopy permits the qualitative identification of the etherifying alcohols and a quantitative estimation of the alkoxy groups present [37]. One of the problems first encountered with the application of GPC to melamine condensates was the low solubility of the product in the organic solvents. This problem was solved by Braun et alia [38-41] by selective silylation of the methylolmelamine.

A solution of methylolmelamines by reaction with N-diethyl-trimethyl-silylamine yield silylethers which are soluble in organic solvents. Only OH groups react during this mild and selective silylation. Due to the silylation of the methylolmelamines gel permeation chromatography in organic solvent is possible: the hydrogen bonds are removed and the difference of the molecular weights of the methylolmelamines becomes larger. Using GPC on a preparative scale [38] all the six polylethers of mono to hexamethylolmelamine were isolated and characterised The trimethylolmelamine silylether could be obtained in its symmetrical form only and the dimethylolmelamine silylether only as the isomer with two monomethylolated amino groups. From the isolated silylated methylolmelamines the six unmodified methylolmelamines were isolated, for the first time. In a later paper [40] GPC was used for a quantitative investigation of the course of the NaOH catalysed methylolation of melamine and the characterisation [42] of two unmodified commercial melamine formaldehyde resins.

NMR and IR spectra of fractions obtained by GPC showed that in resins prepared by condensation in alkaline medium, oligomers are formed containing melamine units bonded by methylene-ether links.

In 1979, Braun and Pandjojo published papers [42-43] in which GPC separation of uncured melamine-formaldehyde-condensates was achieved without any modification of the sample. The solvent used was DMF $N_1$N-dimethylformamide and the effect of the reaction conditions on the rate of condensation was studied. In Japan, two years after the publication of the works of Braun and Legradic,, the six silylated mononuclear methylol melamines were separated by GPC using polyetyrene gel [44] and methylated mononuclear methylol melamines by reverse-phase chromatography using a silica column in acetonitrile-water [45].

GPC was used with $^1$H-NMR for the identification of the different species of methylolmelamines and determination of the molecular weight of the resins in the works by Feurer et alia [46, 47]. They calculated the chemical shifts for mono-di-tri methylol melamine, providing important information for an easier interpretation of $^1$H-NMR spetra of melamine-resins.

Using similar techniques Tomita [48] determined the equilibrium constants and rate constants of the individual addition reactions between melamine and formaldehyde. In this study NMR spectroscopy and high speed liquid chromatograph were used. The latter was applied to the quantitative analysis of methylolmelamines and to determine the free formaldehyde contents in the reaction mixture. The data indicated that the methylolation of melamine nuclei became increasingly more difficult with an increase in the mean degree of addition. This result confirms the studies of Gordon [26]. All of the nine methylolmelamines, including two isomers of di, tri and tetramethylolmelamine could be assigned.

In 1979, Kambanis [49 ] described a technique for the determination of the formaldehyde to melamine ratio by means of an elemental carbon nitrogen analyser. Etherified resins require additionally an NMR spectrum of the analysed sample because in this case some of the total carbon content originates in the alkyl group. The NMR determination of the relative amount of formaldehyde carbon in the etherified resin was reported with a relative error between 2% and 4%. $^1$H-NMR spectroscopy was also combined with chemical analysis to characterise amino resins [50, 51, 52]. By this method it is possible to determine the content of methylol ($-CH_2OH$), methylene and oxymethylene formaldehyde ($N-CH_2-N$, $-CH_2-O-$) and of non substituted ($R-NH_2$), monosubstituted (R-NH-) and disubstituted (R-N=) amino groups. The structural changes that occur during the condensation reaction were followed [52] and it was found that in mild acidic conditions the reactions take place via the formation of methylene linkages ($-N-CH_2-N-$) whereas in mild alkaline conditions the reaction proceeds with the formation of methylene ether bridges ($-N-CH_2OCH_2-N-$). The content of total and combined formaldehydes, methylol, non substituted primary, monosubstituted secondary and disubstituted tertiary amino groups in melamine-formaldehyde resins can be determined using $^1$H-NMR without any chemical analytical method with an accuracy of about 10% [56].

In recent years more attention has been paid on the potentialities of $^{13}$C-NMR spectroscopy, as a strong and reliable tool for the analysis of formaldehyde resins [53]. That is so because $^{13}$Cspectra are rich in information and the signals are sharp and easily identified. There are more distinguishable environments for the carbon nuclei than for protons. This makes H-NMR spectroscopy more limited tool for analysis since the spectra reveal broad and widely overlapping signals suggesting only a few distinguishable environments [54]. The range of $^{13}$C-NMR is about twenty fold that of $^1$H-NMR. De Breet applied $^{13}$C-NMR to the analysis of formaldehyde resins. The spectra were interpreted with the aid of spectra of reference compounds and simple calculations based on the additivity increments. No attempt has been made to assign every line in the spectrum but all different kinds of carbon atoms could be grouped with the help of simple additivity relationships (Table 2.10 ). Alvarez, examined products of the melamine/ formaldehyde reaction using the same technique. The objective was to study the addition stage (methylolation) and get a quantitative interpretation of the results. The spectra were obtained from 30% solutions of monomethylol melamine and hexamethylol melamine in dimethyl sulphoxide (DMSO), and for samples with ratios of formaldehyde to melamine of 2 and 3. A multiplicity of peaks were observed in the spectra of the four mixtures which lead to the conclusion that decomposition of the starting materials yielded equilibrium mixtures of all the 9 methylolmelamine. The results confirmed the measurements of Gordon et al [26, 55]. The $^{13}$C-NMR shifts codes and reasons for the assignments were reported.

The assignments given by Alvarez agree with those given by de Breet with the exception of the bands in the ring carbon region.

The chemical structures of melamine-formaldehyde resins, methylated melamine-formaldehyde resins and melamine-urea-formaldehyde resin were investigated by $^{13}$C-NMR, and the signals of the spectra corresponding to methylol methylated methylol groups and methylene and dimethylene ether linkages were assigned by Tomita

[18].

Recently field desorption mass spectrometry was applied to analyse chemical structures of constituent molecules in methylated melamine formaldehyde resins [57].

Table 2.10 - Chemical Shifts of Carbon Atoms in Melamine formaldehyde Resins [53]

| Observed (ppm) | Assignment |
|---|---|
| 167.4 | $> \mathbf{C} - N\ (CH_2OCH_3)_2$ |
| 166.7 | $> \mathbf{C} - NH\ CH_2OCH_3$ |
| 166.3 | $> \mathbf{C} - NH\ CH_2OH$ |
| 165.7 | $> \mathbf{C} - NH_2$ |
| 77.3 | $> C - N\ (\mathbf{C}H_2OCH_3)_2$ |
| 72.9 | $> C - NH\mathbf{C}H_2OCH_3$ |
| 69.9 | $> C -NH\ \mathbf{CH_2}O\mathbf{CH_2}\ NH - C <$ |
| 64.7 | $> C - NH\ \mathbf{C}H_2OH$ |
| 55.4 | $> C - N\ (CH_2O\mathbf{C}H_3)_2$ |
| 55.0 | $> C - NH\ CH_2O\ \mathbf{C}H_3$ |
| 49.3 | $\mathbf{C}H_3OH$ |

## 2.5 Chemical Methods of Analysis

The literature survey on instrumental methods of analysis of melamine resins reveals a vast number of recent techniques that are liable to influence the studies in this field. But the production of urea-resins for commercial purposes started in England as long ago as 1925 [3], after a patent by Rossiter [58].

Melamine resins were introduced about ten years later. At that time sophisticated methods of analysis were not available and the quality control of the resins produced was empirical and of qualitative nature. With the passing of the years some quantitative methods were established for the analysis of the resins. These methods are normally based on titration procedures and they are time consuming. The analysis of one type of resin may take more than one day of laboratory work, the repeatability of the results is questionable and the analysis of functional groups is limited. However, even with a weak tool of analysis substantial progress in the chemistry of amino resins was noticed in the 50's and 60's and a better understanding of the reactions involved in the manufacture of melamine resins was achieved. Several chemical methods of analysis have been used for the identification of functional groups.

For the determination of nitrogen and, therefore, the melamine content of the resin, the Kjeldahl method is normally used [Appendix 2]. The resin is decomposed by means of sulphuric acid. The decomposition product of the nitrogen, ammonia, is distilled from its solution in the acid after making the solution alkaline, collected in bromide acid and determined by titrating the distillate with standard acid [59, 60]. This method is a very well established analytical method and has been applied for several decades with good results. In order to follow the course of the reactions in the production of melamine resins it is necessary to determine the amount of formaldehyde that reacted. This is done in an indirect way by calculating the total formaldehyde of the solution and subtracting the free formaldehyde in solution. Therefore, the determination of formaldehyde involves two chemical methods of analysis. The content of total formaldehyde in the resin is ascertained by hydrolysis of a sample (1 to 2 g) with phosphoric acid at 110°C. The resin decomposes completely and cyanuric acid is formed from the melamine. All the bonded formaldehyde of the resin, no matter in which form is released to be distilled over with steam. To the aliquot is added iodine solution and thereafter titiated with sodium thiosulphate. The content of free formaldehyde is normally done using the sulphite method (Appendix 2).

The reacted formaldehyde originates from three different kinds of functional groups in the resin structure: methylol groups ($(-CH_2OH)$), condensation bridges ($(-CH_2-$ methylene bridge and $-CH_2OCH_2-$ methylene ether bridge) and butoxy groups ($(CH_2OC_4H_9)$). In order to have a better picture of the structure of the resin it is necessary to determine the butoxy content of the resin. That can be implemented in many ways, but Firth [61] used the Zeisel method with a 2 hour boiling period [60]. Knowing the formaldehyde/melamine ratio and butoxi/melamine ratio, Sreeves [62] presented a method that, based on assumptions regarding the nature of the linkage between melamine units, allows the calculation of the most important functional groups of butylated formaldehyde melamine resins. This method is described in section 4.2.1.

Some analytical methods have been described for the estimation of free methylol groups in organic solvents [63-65]. Van Zuylen used the reaction of formaldehyde with dimedone to calculate the methylol content of different kinds of resins with good results.

## 2.6 Combined Instrumental and Chemical Methods of Analysis

The Working Party on Supported Polymer Films (SPF) of the Macromolecular Division of IUPAC has performed an inter-laboratory study concerning the analysis of functional groups in amino resins, in particular urea and melamine resins used in the coatings industry [66]. "As an introduction a literature study on analytical procedures was carried out aiming at a survey of the most applicable methods for analysis of the most important functional groups in amino resins" [67]. Based on this survey four methods were selected and tentative descriptions were drafted and discussed in detail among some of the participants. Seven samples comprising two urea derivatives, two melamine derivatives and three commercial amino resins, were selected for the cooperative testing of the tentative methods. The four model substances, two urea and two melamine derivatives, were characterized by independent techniques. The tentative method, tested in the inter-laboratory excercise, have been improved and rewritten as Recommended Methods considering all the critical remarks and comments to the tentative methods. These recommended methods can be found in Appendix 3.

From the literature survey Christensen reached the following conclusions:

1. "There is a need for a method for the removal of solvents from resin solutions in such a mild way that the structure of the actual amino resins remains unchanged in order to isolate the resin solids to be used for subsequent analysis of the functional groups. Such a method also enables the non-volatile content of amino resin solutions to be determined.
2. By means of $^1$H-NMR spectroscopy it should be possible to identify and determine the common alkoxy groups in urea and melamine resins. It seemed likely that $^1$H-NMR spectroscopy would be generally applicable for the determination of methylol, imino and amino groups also. Apparently the quantitative determination of functional groups could be either a combination of $^1$H-NMR spectroscopy and chemical analysis of total formaldehyde or $^1$H-NMR spectroscopy alone with the use of an internal standard.
3. Alkoxy groups could be analysed both qualitatively and quantitatively by transetherification followed by gas chromatography of the liberated alcohols corresponding to the alkoxy groups.
4. Alkoxy groups could also be analysed both qualitatively and quantitatively by Zeisel cleavage followed by gas chromatography of the liberated alkyl iodides corresponding to the alkoxy groups.
5. 13C-NMR spectroscopy should be a rather powerful technique for the qualitative analysis of the functional groups in amino resins.

6. Special titrimetric procedures could be used for the determination of methylol groups in some amino resins, but generally applicable titrimetric methods were unknown".

Based on these conclusions, four tentative methods were designed by specialists to be applied to the 3 commercial resins.

Eight different laboratories from different countries took part of the exercise of analysing the four model compounds and three commercial resins. Based on the results obtained the recommended tests (Appendix 3) were established. The following conclusions were reached:

"Method no 1 - Solvent removal from amino resins" is a practical technique for the determination of the solids content of amino resins and for isolating resin solids to be used for subsequent analysis. The repeatability i.e standard deviation within laboratories, is about 0.4 wt%.

"Method no 2 - Analysis of urea and melamine resins by H-NMR spectroscopy" is a useful method for qualitative and quantitative analysis of functional groups in the resin. However, imino and methylol groups in butylated urea resins cannot be analysed with a satisfactory accuracy. For the other functional groups in question, e.g alkoxy groups in urea and melamine resins, imino and methylol groups in melamine resins, the repeatability is 0.3-0.4 mol functional group per kg resin.

"Method no 3 - Analysis of alkoxy groups in amino resins by transetherification followed by gas chromatography" is a simple technique for qualitative and quantitative analysis of alkoxy groups. For analysing mixtures of alkoxy groups this procedure is better than the $^{1}$H-NMR technique. The repeatability for methoxy groups and butoxy groups is about 0.2 and 0.1 mole per kg resin respectively.

"Method no 4 - Analysis of alkoxy groups in amino resins by Zeisel/Merz cleavage followed by gas chromatography' is a relatively simple technique for identification and determination of alkoxy groups. It is not possible to determine iso-butoxy groups quantitatively by this technique. However, for methoxy and n-butoxy groups the repeatability is similar to the transetherification procedure $^{13}$C-NMR spectroscopy is a remarkable technique regarding qualitative analysis of functional groups in amino resins. Mixtures of alkoxy groups are easily identified by this technique.

It is apparent that there has been a very considerable effort to unify standard methods for the analysis of amino resins. The work just described is a proof of this. In the past the methods of analysis were limited to chemical methods of analysis implemented in the laboratory. With the development of chromatography and spectroscopy, more detailed analysis was possible, and these techniques were used on their own or combined with chemical analysis to the study of melamine formaldehyde reactions. The time it takes to study or analyse a resin has been reduced and the techniques have made it easier to accomplish the task. However, as far as production is concerned the development has been slow.

Usually, powerful analytical techniques, such as ultraviolet or infrared spectroscopy, do not fit into a production facility such as the manufacture of butylated formaldehyde melamine resins. Most analysts would be horrified by the prospect of resin and oils dripping over their optics. Differential chemical analysis and dielectric measurements seem to be serious candidates to fill the gap between laboratory and works environment [68]. Differential thermal analysis is a technique for determining the properties of materials from the thermodynamic and kinetic points of view. Dielectric measurement is also a powerful tool for probing the structure of materials. It measures the dipole response within dielectric materials to an applied electric field. Spatial arrangement and viscoelastic properties of dielectric materials are the two major factors of dipole response. Differential thermal analysis is being increasingly used in research and process control, offering the advantages of being non-obtrusive and easily instrumented (an electric field can be easily wired into almost any place). When dielectric analysis is run concurrently with differential thermal analysis properties like polymeric crosslinking behaviour, molecular weight increases and viscoelastic behaviour can be studied. Other quality control control tests used in the manufacture of butylated formaldehyde melamine resins are described in section 3.5.

# CHAPTER THREE

# INDUSTRIAL AND LABORATORY PROCESSES

# 3 INTRODUCTION

In this chapter a description of the industrial and laboratory processes for the manufacture of butylated formaldehyde melamine resins will be presented giving special attention to the similarities and differences of the process in the two different environments: laboratory and factory.

From the comparison and discussion of the processes some general ideas for the pilot plant rig design were achieved. However, detailed information for the design of the pilot plant apparatus will be given in Chapter 5. Due to differences in the design and scale of the several plants, some differences in their operation also appeared. An operation procedure will be given for the laboratory scale equipment. The instructions for the operation of the pilot plant will be discussed in Chapter 6. This chapter ends with a survey of the quality control tests and analytical methods used in industry during manufacture of the resin or after a batch for the characterisation of the product.

### 3.1 Laboratory Process

In order to gain some insight into the process, two laboratory experiments were done in industry. In both experiments a clear resin was manufactured, with properties according to the required specification. The sub-sections that follow are a description of these two experiments, with the log sheets of the progress of each experiment in Appendix. 3.

#### 3.1.1 Description

Butylated formaldehyde resins may be made by various techniques but the method most often used is as follows. Melamine is first dissolved in neutralised formalin, excess butanol and a small amount of an entraining agent· usually xylol or white spirit are introduced into the reaction vessel and water is removed azeotropically using a decanter system similar to that shown in figure 3. 1. The azeotrope which distils over at a temperature of 92°C (i.e, well below the boiling point of n-butanol) condenses and separates into two layers. The upper layer, containing butanol, xylol and a little water, is returned to the reaction vessel; the lower layer consisting of water and some butanol dissolved in it, is withdrawn as necessary. When most of the water has been removed, an acid catalyst, a solution of phthalic anhydride in butanol, is added and azeotropic distillation continued. Butylation of $-CH_2OH$ groups occurs concurrently with various condensation reactions to produce eventually a clear colourless resin of required organic solvent tolerance and viscosity. As the degree of butylation is increased the viscosity and reactivity of the resin falls, whereas the stability and compatibility with both solvents and other resins increase. For this reason, great care must be taken during manufacture to balance the amount of resinification and the degree of butylation.

In practice, a range of products is made available so that a resin with the correct combination of properties can be chosen for a particular application. C.P Vale(120) describes an experiment, illustrating the chemical nature of the products obtained during the previously described technique.

### 3.1.2 Operation

The reactants charge for a 2 litres volume reactor is given in table 3.1.

| | Molecular Weight | Molar Ratio | Charge |
|---|---|---|---|
| Melamine | 126 | 1 | 252 g |
| 36% w/w Formalin | 30 | 6.2 | 867 g |
| N/Butanol (1) | 74 | 4.5 | 666 g |
| Xylol | | 48 $cm^3$/ mole mel | 96.0 $cm^3$ |
| N-Butanol (2) | 74 | 0.9 | 133 g |
| Acid Catalyst | | 2.8 $cm^3$/ mole mel | 5.6 $cm^3$ |

Table 3.1 Resin manufacture - a typical charge.

Manufacture Instructions

1. Adjust pH of formalin to 5.6 - 6.0 with minimum amount of N/1 NaOH. Charge formalin.
2. Charge melamine and butanol.
3. Heat to reflux in about 30 minutes.
4. Hold at gentle reflux for 15 minutes
5. Charge xylol over 15 minutes and begin to distil at 50 ml/mole melamine per hour.
6. Charge butanol (2), 3 hours after xylol.
7. Charge catalyst when distillate off is 280 ml/mole of melamine. After catalyst addition do not increase heat input but allow rate of water removal to decrease naturally.
8. Process to a specified white spirit tolerance and PRS viscosity.
9. At the correct tolerance, cool resin to 60°C and concentrate to a specified viscosity at a vacuum of 25" Hg.
10. Filter resin while warm.
11. Check properties of finished resin - PRS viscosity, solids content acid value and white spirit tolerance.

Following the instructions just described two laboratory experiments were done. The log-sheets are presented in Appendix 3.

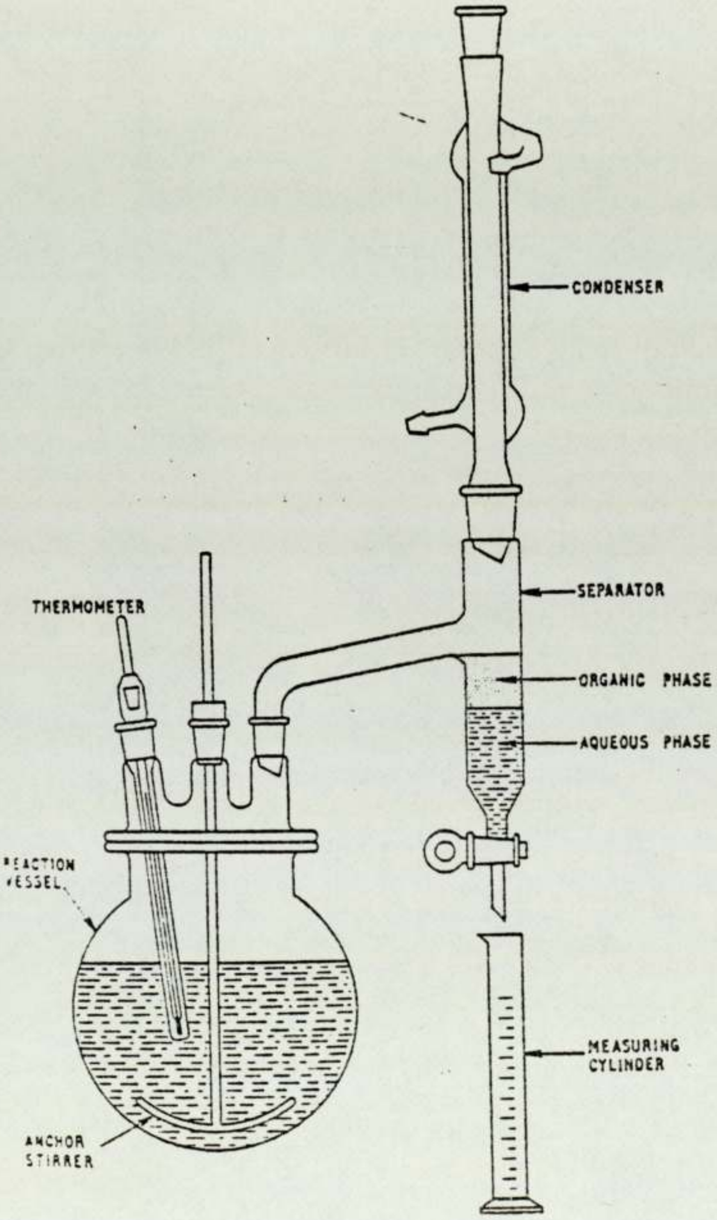


Figure 3.1 The Preparation of Butylated Amino Resins (120).

The two experiments progressed as expected and the resin obtained had perfectly acceptable properties. Looking at the final specification of the products one can say that some overcooking took place. Although, the viscosity and acid value being well inside the specification range the solvent tolerance and solids content values are slightly high which proves that both conservation and butylation reactions were taken too far, and the batch should have finished half hour earlier. One can also conclude that the right balance between the two reactions was achieved.

## 3.2 Industrial Process

The industrial process of the manufacture of butylated and melamine formaldehyde resins, can be regarded as the laboratory process on a larger scale. A brief description of the equipment involved will now be given.

### 3.2.1 General Description

The process to be described is based on the resin manufacture at British Industrial Plastics. The batch reactor was constructed in stainless steel so as to maintain a high corrosion resistance. Heat is supplied to the still via a well lagged heating jacket using steam at a pressure of 2.5 bar. This is supplemented by a heating coil element found within the still.

The still contents are constantly mixed using an agitator of the straight arm paddle type. The top of the reactor is fitted with a pressure relief vent with a flame trap assembly, a wet butanol recycle line and a distillation column. The final product is discharged through a positive displacement monopump and filtered via a Johnson filter press to storage. The vapour from the reactor pass to a distillation column which is a well lagged stainless steel unit. It is packed with rings for operation under low pressure drop condition. The lower volatility components pass back down the column to return to the reactor while those of a high volatility travel through a large bore pipe to be condensed. The condenser also made in stainless steel is vertically adjacent to the distillation column. Vapour enters the condenser from the distillation column and sufficient heat is removed from it by a stream of cooling water to ensure that the leaving components are in liquid form. Following the condenser, there is a buffer tank also constructed in stainless steel, with a capacity of 190 litres. It is intended to regulate the flow of the separator and to enable reflux of the condensate which is now well mixed for use as reflux to the distillation column via a positive displacement pump.

After the buffer tank there is a separator whose main function is to separate the heterogeneous mixture into two phases: an alcoholic phase which is recycled to the reactor and an aqueous phase which is removed from the system. This separation is possible because of the difference in densities of the two phases and their degree of miscibility. It has a fine inner packing to promote a high interfacial area between the two phases and a higher degree of turbulence in the fluids resulting in a high mass transfer rate. There is a filter press which holds back any solid impurities entrained in the resin and allows the clear resin to pass through. The filtrate is normally recycled until the required clarity is met. These are the main pieces of equipment used for the manufacture of butylate and formaldehyde melamine resins in industry and they are shown in Figure 3.2.

### 3.2.2 Raw Materials

The still charge is given in Table 3.2

| Raw Materials | Quantity |
|---|---|
| Melamine | 1075 kg |
| Formalin 44% | 603 gallons |
| or " 36% | 743 gallons |
| N-Butanol (1) | 763 gallons |
| N-Butanol (2) | 160 gallons |
| Xylol | 90 gallons |
| Acid Catalyst | 2.7 gallons |
| Antifoam solution ½% | 500 ml. |
| 70% + W Caustic Soda Solution | 500 ml. |
| Perlite Filter Aid | 6 kg. |

Table 3.2 Resin - Raw Materials

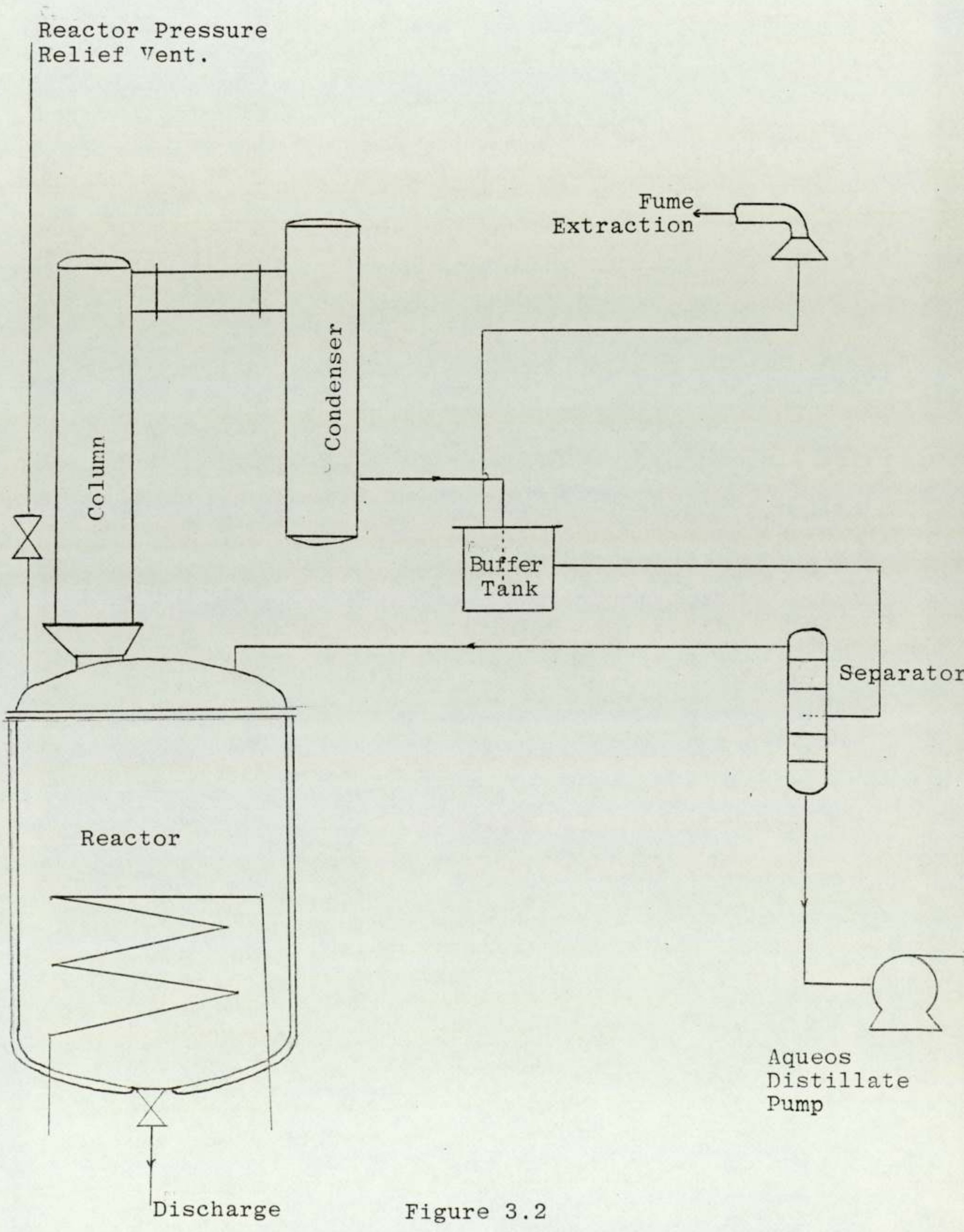


Figure 3.2

Industrial Production of Melamine Formaldehyde Resins.

## 3.3 Comparison of Laboratory and Industrial Equipment

It is interesting to investigate the reason why results in terms of final product quality often do not coincide in the laboratory and in the works. It is apparent that there exist differences in heat transfer efficiency, being relatively small on the works scale. There, the temperature rise is slow resulting in longer residence time of the reaction mixture in the reactor. This factor is related to the agitation system in both environments. In the laboratory we are dealing with a 2 litres reactor, relatively small, and the agitation power per litre of resin is much higher in the laboratory scale. In the works, the reactor is much bigger and the stirring system is not correspondingly powerful to give the same degree of agitation.

Another obvious difference between the two operation procedures concerns the value of pH at which formalin is adjusted at the beginning of the batch. Firth (119) did some work on this subject and concluded there were no significant differences in properties over the formalin pH range 4.6-5.9. However, samples made with the formalin at lower pH, 4.1-4.4, had a noticeably higher viscosity and were less susceptible to butylation. The syrup in the beginning becomes inhomogeneous about 15 minutes after the xylol has been added and remains so for about 4 hours. This effect is always held to be undesirable. As a result of that investigation the manufacturing procedure of the industrial scale was amended and formalin started to be adjusted to PH 5.6-5.9. That implied a correction in the amount of acid catalyst used for the acidification stage, that was adjusted to a value of 2.8 ml per mole melamine. There is also some difference in the procedure of adjusting the pH of formalin in the laboratory and on the plant.

In production, normally a fixed quantity of sodium hydroxide was added to the formalin and the pH was adjusted to the required value with formic acid, instead of using the minimum possible amount of sodium hydroxide, as it is done in the laboratory. Firth studied this problem and reached the conclusion that the viscosity-solids relationship of the resin was altered by that factor. The procedure used in the industrial process would lead to a high viscosity product and a loss of reactivity of the resin was noticed.

Therefore, the procedure recommended for adjusting the pH of the initial formalin is to use the minimum amount of sodium hydroxide.

Apart from the difference just mentioned, the two processes, laboratory and production, follow the same kind of pattern, with slight differences in the temperature of the separator. This difference was analysed by Firth and the effect on resin properties was found negligible.

## 3.4 General Ideas for the Design of a Pilot Plant

From the visits to industry, and for the work in the laboratory and plant, a lot of background information was acquired. The objective was to get the necessary information so that a pilot plant rig could be built at Aston University, where the experiments were carried out with the help of a computer, one of the facilities of the Chemical Engineering Department. A more detailed description of the pilot plant equipment and operation will be given in Chapter 5. A certain number of ideas can however be taken, now.

1. The process follows a sequential series of operations. Two stages of the process are perceptible: First stage that includes starting up the plant and the other operation up to acid catalyst addition. At this stage no samples are taken and no information about the resin quality exists. Second stage, after the acid catalyst addition, where butylation and condensation reactions are competing. The former has a clear influence on a quality test mentioned in next section, solvent tolerance test, and the last is a determinant of the viscosity of the resin. Because the final product specification depends on the correct balance of these two reactions, it is very important to monitor the quality of the resin at this stage. That is one of the reasons why some samples are taken regularly to make sure that gelation does not occur. Gelation occurs when there is over-condensation, and very little butylation of the resin. That can be measured partially by the variation of the viscosity of the resin at this stage of the process. Since a syrup with high viscosity shows an incorrect balance between condensation and butylation, an effort should be made to alter

the relative rates of the competing reaction. Firth studied the effect of certain plant and process variables on the resin properties. He showed that it was necessary to add butanol to achieve the required viscosity level and the finished resins were more viscous than usual (119). He concluded that the addition of butanol prevents gelation, but the solids content of the syrup is reduced and it did not compensate for the use of an unsatisfactory starting formulation". This conclusion shows how important is the initial change of the raw materials, the quality for the formalin used and the adjustment of its pH. Another two stages of the process can also be detected after having reached the required solvent tolerance. These are: third stage where the viscosity is adjusted to the desired final value. It consists essentially of the removal of the excess solvent by distillation under vacuum. The fourth stage consists of filtering the final resin until the clarity standard is met. These two final stages are only important for commercial production and they will not be studied in this work. If the resin at the end of stage two is within the specification range, then in the final two stages the desired product will be certainly obtained. Therefore, as far as the manufacturing process is concerned, only the first two stages really matter, and they will be the ones looked at in the pilot plant rig.

2. The second observation taken from the laboratory work and industrial process is the lack of any quality test of the resin in the first stage of the process. In this stage a great deal of water is being removed from the reactor and it is almost certain that the three main reactions are taking place. The fact of not taking any quality test at this stage is related to the difficulty of getting accurate analytical measurements of the reactor, contents, since when a sample is taken two phases appear: one solid phase mainly a mixture of methylol melamines, polymers formed by condensation butylated or not and a second phase constituted essentially of solvent, i.e, xylol, butanol, some unreacted formaldehyde and water. We will come back to this point in the next chapter.
3. It is apparent that there is a difference in the amount of time it takes to make a batch of resin in the laboratory or in the works. It was noted that the water removal in the first stage of the process is faster in the laboratory as well as the increase of solvent tolerance of the resin in the second stage. That can be attributed to the differences in heat transfer efficiency in the laboratory production. For the pilot plant rig, and due to a different design of the plant, the time of each run could be shortened.
4. Samples are taken in the second stage of the process. Therefore a sampling line must be part of the pilot plant rig.

5. The toxicity of formaldehyde and flamability of butanol will have to be taken into account in the design of pilot plant rig.
6. The use of xylol as an entrainer needs some clarification. One of the difficulties encountered in the manufacture of butylated formaldehyde-melamine resins is the need of extracting the water introduced in the reactor due to the use of formalin solution, 36% w/w as the formaldehyde source. As it is well known, butanol and water form an azeotope (121). That constitutes the main stream coming off the distillation column at the top of the reactor. When this stream is cooled in the condenser and gets to the separator it splits in two phases. One alcohol rich phase, mainly butanol and water, and an aqueous phase constituted essentially of water with some butanol dissolved in it. If some xylol is added to the mixture in the reactor the vapour at the top of the distillation column will contain some xylol, that after cooling will displace some water from the alcoholic phase. Therefore, the alcoholic phase is essentially xylol and butanol and little water and the aqueous phase constituted of water with some butanol dissolved and without any xylol. This was confirmed by the work of Cadman (118) who studied the effects of varying the entrainer content of the batch. The effect of the entrainer can be particularly important at the end of the second stage when most of the water has been removed from the still and the small amount of water coming from the recycle of the alcoholic layer may influence the butylation reaction rate of the

resin. In fact both reactions, condensation and butylation release one molecule of water. However, due to the reversibility of the later reaction, the water present in the reactor has a negative effect on the degree of butylation obtained. The amount of xylol used in the laboratory and works agree and there seems no point in changing the xylol charge for the pilot plant experiments.

7. The first stage of the manufacture of the resins ends with the addition of the acid catalyst, monobutyl phatalate. The instructions for the right time to add the catalyst are not the same in the laboratory and at the works. For the first case, the catalyst is added when the water introduced as formalin has been removed from the process whereas in the industrial production it is said to add the catalyst when the temperature in the reactor reaches 100°C. In fact, these apparent contradicting instructions are saying the same thing in two different ways because when the water removed from the process reaches the value of the water introduced as formalin the temperature in the reactor is approximately 100°C. The addition time of the catalyst was found by Firth to be an important factor in the properties of the final resin. He showed (118) that "an early charge into a reaction mixture with a high water content, led to a more viscous product, with the opposite effect being noted when charging was late". Therefore, the amount of water in the reaction vessel at the time of the acid addition is an important factor in the production of butylated melamine formaldehyde.

Firth in his research changed the catalyst charge size as well. He found that a clear relationship exists between the catalyst charge and the viscosity of the finished resin: the larger the charge the higher the viscosity. That proves that the catalyst is not only an etherification catalyst but it also promotes the condensation reaction. The catalyst addition time and the size of the catalyst charge are two important factors that have a marked effect on resin properties and therefore require careful control.

The information based on the experience acquired in the laboratory and on the observation of the industrial process gave the necessary background for an effective design of the pilot-plant equipment discussed in chapter 5. It also gave a good insight of the chemical reactions taking place during the manufacture of the resin and of the factors that can influence the balance of condensation and butylation reactions, i.e the properties of the final resin obtained.

### 3.5 Quality Control Tests

It was mentioned in point 4 of the previous sections, that samples are taken in the second stage of reaction. At the moment a certain amount of resin is taken from the reactor at regular intervals so that some quality control tests can be performed to monitor the resin's properties. The description of the tests performed by BIP during a run both on the production line and laboratory is given in appendix 1. Due to the time consuming nature of the quality control tests performed and large batch to batch variations in the results, it has been quite difficult to find ways to automate them and they are performed at the moment off-line and manually. Some work has been done by Mouzakis,(122), to test the practicability of a system of continuous resin circulation and in-line sample analysis outside the reaction vessel. He examined some variables that hopefully could be useful control variables for monitoring the progress of the two competing reactions. These variables to be useful have to change during the amino coating resin manufacture in a distinct and sensitive way, increase or decrease in a similar fashion during each batch, so that they can provide coherent, speedy and reproducible readings. The first variable to look at is obviously viscosity. It was found (123) that batch to batch variations are quite large making it a rather vulnerable possible control parameter. A viscometer is however a useful in-line testing system, for safety reasons (danger of gelation) and it also would facilitate viscosity adjustments at the end of a process. Many hardware configurations for continuous viscosity measurements fall into four categories, the rotational-type, the float or piston type, the vibrating probe type and the capillary type (124). Mouzakis in his experiments used a falling sphere or mixing bubble viscometer of the float type category. He manages to get a measurement device that although not being continuous provided measurements at adequate small time intervals. Due to the doubtful value of viscosity as a control variable, and the expansive equipment that involves to have a continous measurement device, it was decided to measure viscosity in the pilot plant the same way it is done in industry that is, using standard PRS viscosity tubes and measuring the time it takes a bubble to travel from bottom to top of the tube when the resin is at 25°C.

Another property to look at carefully is solvent tolerance that provide us with a measurement of the progress of the butylation reaction. In fact as butylation reaction proceeds, resin molecules become increasingly more susceptible to solvation and tolerance towards white spirit, xylol or heptane increases while towards methanol decreases. The solvent tolerance test, involves a turbidity measurement and therefore a titration, (see appendix 1). To get this measurement automated some technical problems have to be solved;

1. The samples taken are to be consumed because of the titration and that causes a reduction of the batch size at least in the laboratory scale if performed continuously.
2. Large quantities of solvent would be consumed in a continuous measurement.
3. The operation of weighing the resin sample in a continuous measurement is difficult.
4. The operation of waste disposal and washing the container for repetetive titration, is a problem due to the sticky nature of the resin.
5. Adequate mixing of a viscous resin sample at a constant temperature (20°C) during the titration are difficult to achieve.

It was decided to implement the tolerance test in the pilot plant as it is done in industry, ie, titration and turbidity test done manually.

Solids yield is another quality control test that can provide a measurement of the degree of condensation which can vary among batches with equal viscosity. Small solids yield indicates high molecular weight of resin molecules. That suggests that this test could be used as a parameter on the process. However, looking at the instructions of the test (appendix 1), it is clear that it involves accurate weighing of the sample and two hours of heating at a constant temperature oven. The solids yield is normally done in the end of the batch when the final properties of the resin are assessed.

## 3.6 Analytical Methods

The analytical methods used for the determination of functional groups of the resin structure are an important tool for the study of the reactions taking place in the manufacture of amino resins. A certain number of papers have been published recently about this subject and they have been discussed in chapter 2.

The methods used in BIP for the characterisation of the chemical structure of the resins are described in appendix 2. They provided us with the necessary information to set up a kinetic model of the reactions occuring in the manufacture of butylated formaldehyde melamine resins, that will be discussed in the next chapter.

# CHAPTER FOUR

# KINETIC SIMULATION MODEL

## 4.1 INTRODUCTION

In this chapter a kinetic simulation model is established for the chemical reactions involved in the manufacture of butylated formaldehyde melamine resins. The lack of literature suitable for the complete characterisation of the reactions has already been mentioned in chapter 2. However, this lack of studies is not evenly distributed for all reactions involved in the resin manufacture. There is quite a large number of papers concerned with the methylolation reaction but they are not of much use for this study since normally they refer to conditions of medium different from the ones under study. In the published literature methylolation is normally studied on its own and because of that the authors try to isolate the reaction from the condensation reactions finding operating conditions favourable to methylolation reaction and hostile to the other reactions. That is the reason why most of the papers, study the reaction at temperatures in the range of 35 to 40°C, causing their analysis to be valid only for the early stages of the reaction. As has been said in chapter 3 the reactor temperature is at its minimum 90°C and therefore it is that range of temperatures that we are concerned with.

For the condensation reactions less papers are available, and the great majority deal with aqueous medium, which is not the case in industrial production, since butanol is present to promote the solvent tolerance characteristics of the resin.

Taking into account the limitations mentioned it was decided to take the following steps:

1. Use information available directly from industry (Firth's report) to establish a kinetic model for the standard change of the batch.
2. To test the suitability of the model for non-standard batches, i.e study of the effect of changes in formaldehyde; melamine ratio and butanol; melamine ratio.
3. To discuss the effect of the chemical structure of the resin on the viscosity and solvent tolerance values.

## 4.2 Chemical Data Available

A description of the operation of a laboratory experiment for the manufacture of butylated formaldehyde resins has been given in section 3.1.2. In order to implement a simulation model it is necessary to present the data on which it was based upon. In this section the chemical data available will be presented and it will be explained how this information has been processed to be of any use for the model. The information that is going to be used is based on Firth's work on butylated melamine resins (114, 115, 116).

### 4.2.1 Relating Parameters from Analytical Methods with the Chemical Structure of the Resin

From chapter 3, section 6, the analytical methods for determination of the concentration of certain important chemical groups in the chemistry of butylated formaldehyde-melamine resins, were explained.

Now it is important to see what the relation is between the concentration of these chemical groups and the actual chemical structure of the resin. This was done by A W Firth in the following way:

Suppose that the following analytical methods were used:

(a) Sulphite method - Determination of free-formaldehyde in resin solution.

(b) Iodometric method following a distillation from aqueous phosporic acid at 110°C - Determination of the total formaldehyde in resin solution.

(c) Kjeldahl method - Determination of nitrogen in vacuum solids.

(d) Zeisel method - with a 2-hour boiling period and allowing the condenser water to boil towards the end - Determination of the butoxy group present in vacuum solids.

Firth in his work used an operating procedure as described in 3.1.2, taking samples of the resin solution, 1, 2, 4, 8 and 16 hours after the acid addition. He first measured the solvent tolerance, viscosity and solid contents of these samples and later used the above analytical methods to determine the concentration of chemical groups of interest for the definition of the chemical structure of the resin. A standard set of results for a resin with the standard ratios melamine-formaldehyde-butanol of 1:5.28:5.35 is given in the table 4.1.

| Sample | Tolerance (ml) | Vacuum solids % | %Nitrogen (on vac sol) | %Melamine (on vac sol) | %Total $CH_2O$ (on resin sol) | %Free $CH_2O$ (on resin sol) | %Combined $CH_2O$ (on vac sol) | %Butanol (on vac sol) | Ratio M:F:Buo |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 5 | 51.7 | 26.1 | 39.1 | 21.8 | 3.0 | 36.4 | 37.3 | 1:3.91:1.62 |
| 2 | 10 | 53.8 | 25.6 | 38.4 | 23.3 | 3.0 | 37.7 | 38.5 | 1:4.12:1.71 |
| 3 | 20 | 59.1 | 24.4 | 36.6 | 24.3 | 2.6 | 36.7 | 39.9 | 1:4.21:1.86 |
| 4 | 32 | 61.1 | 23.2 | 34.9 | 24.2 | 2.4 | 35.7 | 46.3 | 1:4.29:2.26 |
| 5 | 83 | 65.5 | 22.4 | 33.6 | 24.1 | 1.9 | 33.9 | 48.7 | 1:4.24:2.47 |
| 6 | >150 | 69.2 | 21.4 | 32.0 | 25.1 | 1.5 | 34.1 | 52.1 | 1:4.48:2.78 |

Table 4.1 Analytical data for M:F:BuOH = 1:5.28:5.35

Having calculated the M:F:BuO ratios for different samples, Firth went on and related the ratio M:F and M:BuO (f and b) with the chemical structure of the resin as follows:

(a) Assuming methylene ether bridges

Let the average molecular composition of the resin be:

$$(C_3N_6)_n\ (CH_2OCH_2)_{n-1}\ (CH_2OBu)_x\ (CH_2OH)_y\ H_z$$

Since the $C_3N_6$ group is hexafunctional,

$$6n = x + y + z + 2(n-1)$$

i.e $x + y + z = 4n + 2$ (1)

Defining the ratio melamine: combined formaldehyde: butoxy as 1:f:b then:

$$f = \frac{x + y + 2(n-1)}{n} = \frac{x + y - 2}{n} + 2 \qquad (2)$$

and $b = \frac{x}{n}$ (3)

From (2) and (3)

$$\frac{y - 2}{n} = f - 2 - b$$

$$\therefore \frac{y}{n} = (f - 2 - b) + \frac{2}{n} \qquad (4)$$

From (1),

$$\frac{z}{n} = \frac{4n + 2}{n} - b - (f - 2 - b) - \frac{2}{n}$$

$$\therefore \frac{z}{n} = 6 - f \qquad (5)$$

Molecular weight = 120 n + 44(n - 1) + 87n + 31y + z

By substituting for x, y, z, we have

$$\frac{M - 18}{108} = n\,[1 + 0.278f + 0.518b] \qquad (6)$$

(b) Assuming Methylene Bridges

Let the average molecular composition of the resin be, :

$$(C_3N_6)_n\ (CH_2)_{n-1}\ (CH_2OBu)_x\ (CH_2OH)_y\ H_z$$

One can still write

$$x + y + z = 4n + 2$$

and

$$f = \frac{x + y + (n - 1)}{n} \qquad (7)$$

and

$$b = \frac{x}{n} \qquad (8)$$

From (7) and (8)

$$\frac{y}{n} = (f - b - 1) + \frac{1}{n} \qquad (9)$$

$$\frac{z}{n} = 5 - f + \frac{1}{n} \qquad (10)$$

Molecular weight = 120 n + 14(n - 1) + 87n + 31y + z

From table 4.1 and with the help of the equations derived table 4.2 can be constructed.

| Sample | Reaction Time (Hrs) | White Spirit Tolerance (ml) | M : F : BuO | Molecular (wt) | Degree of Polymerisation (n ) | Methylene Ether Linkages |  | Methylene Linkages |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Methylol Per Melamine y/n | Unsubst. Hydrogen Per Melamine z/n | Methylol Per Melamine y/n | Unsubst. Hydrogen Per Melamine z/n |
| 1 | 1 | 5 | 1 : 3.91 : 1.62 | 1350 | 4.2 | 0.76 | 2.1 | 1.5 | 1.3 |
| 2 | 2 | 10 | 1 : 4.12 : 1.71 | 1340 | 4.0 | 0.91 | 1.9 | 1.7 | 1.1 |
| 3 | 4 | 20 | 1 : 4.21 : 1.86 | 1250 | 3.6 | 0.90 | 1.8 | 1.6 | 1.1 |
| 4 | 8 | 32 | 1 : 4.29 : 2.26 | 1340 | 3.6 | 0.58 | 1.7 | 1.3 | 0.99 |
| 5 | 16 | 83 | 1 : 4.24 : 2.47 | 1890 | 5.0 | 0.17 | 1.8 | 0.97 | 0.96 |
| 6 | 26 | >150 | 1 : 4.48 : 2.78 | 2530 | 6.3 | 0.01 | 1.5 | 0.86 | 0.68 |

Table 4.2 Deductions from data of table 4.1

About this data the following comments are pertinent:

1. The values of the tables rely on the results of analytical methods which are time consuming (Zeiss method for example) and not very accurate. Experimental errors necessarily affect the results.
2. This data in particular refers to samples taken after the acid addition, therefore in the last stage of the production of butylated formaldehyde-melamine resin. In the first stage of the reaction the resin solution separates in two phases which makes the analytical methods even more inaccurate.
3. In order to relate the results from analytical methods with the chemical structure of the resin the author had to assume that only one type of linkage was present.
4. The samples were taken from a reaction glass vessel, two litres of capacity and operating as described in 3.1.2. The dimension of the equipment and the conditions in the pilot plant and industrial plant are different from the ones used by Firth in the laboratory.

Having made these comments, it can be asked why to use this data? The answer has to do with the lack of suitable information in the literature. In fact, in spite of the previous comments on this data, it is still the most appropriate to be used The reasons for this are:

1) The proportions of melamine: formaldehyde: butanol used in Firth's work are the ones used in the production of the resin prepared in the pilot plant.

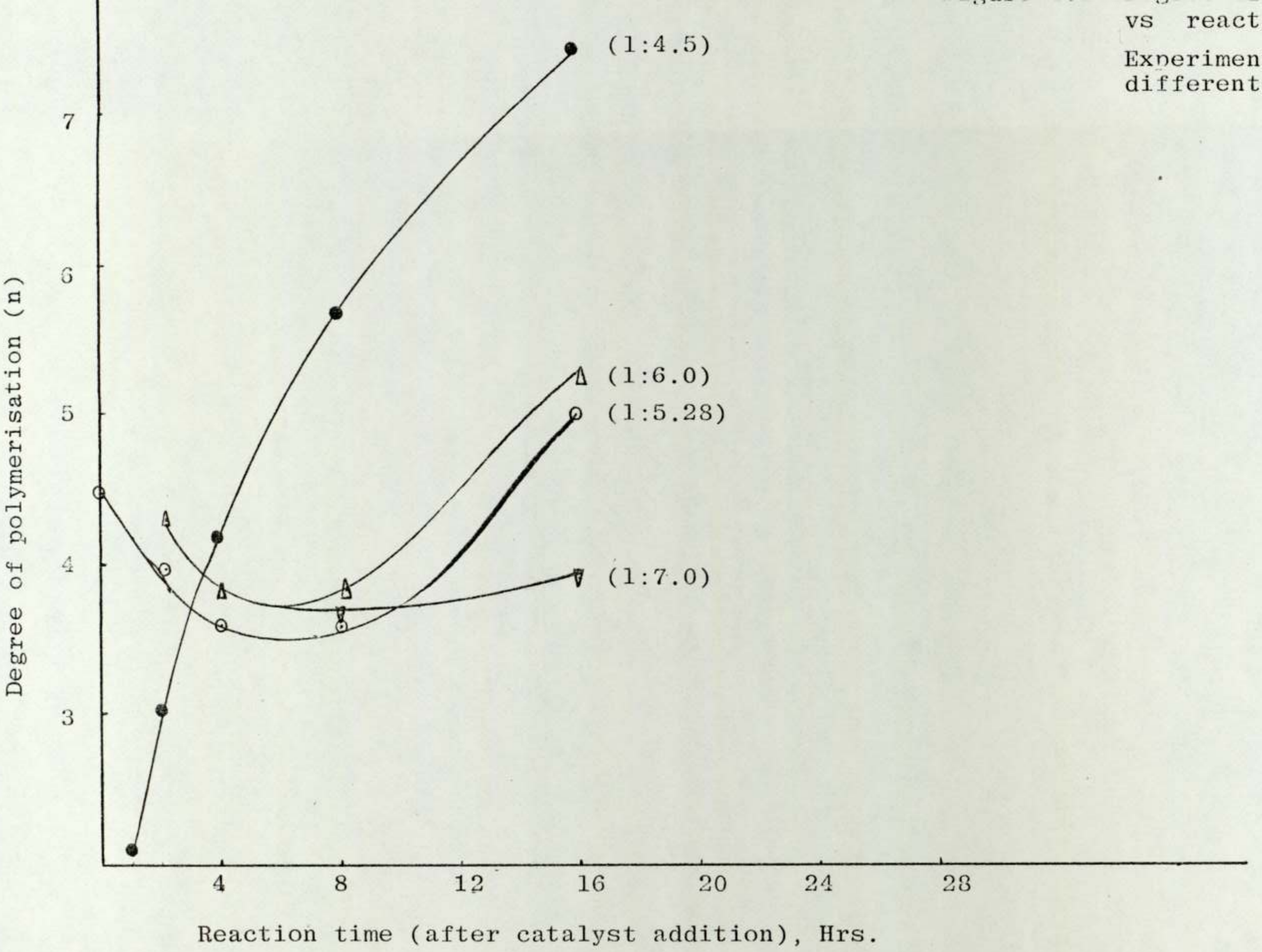
2) The temperature variation during the batch in the pilot plant and industry, agrees with the one in the laboratory.

3) The reaction takes place in an alcoholic medium in all the plants, and most of the data in the literature refers to aqueous medium

4) Data from Firths report is complete, because the author studied the influence of changing M:F and B:M ratios, in the properties of the resin. The results are shown in fig 4.1 to fig 4.12 and they will be discussed in the next section.

### 4.2.2 Some Comments on the Experimental Results of A Firth

1. The polymerisation number, i.e. number of bridges per ring units of melamine shows very different behaviour for different melamine: formaldehyde ratios. In the case of low ratio (1:4.5 - Fig 4.1) the polymerisation degree of the resin increases with the reaction time especially in the first 15 hours. The rate of reaction is high when compared to the other M:F ratios. It is also apparent that for the other ratios, there is a distinct decrease in the degree of polymerisation up to about 6 hours of reaction followed by an increase in the latter stage of reaction. This feature of the polymerisation reaction is very important for the manufacture of butylated formaldehyde melamine resins since the specification is normally met four to six hours after the acid addition. It is obvious that condensation rates like the ones observed for M:F = 1:4.5 mean high viscous resins, low solvent



vs reaction time.

Experimental results for different values of M:F ratios.

reaction time

Experimental results for different values of M:F ratios.

Methylene assumption.

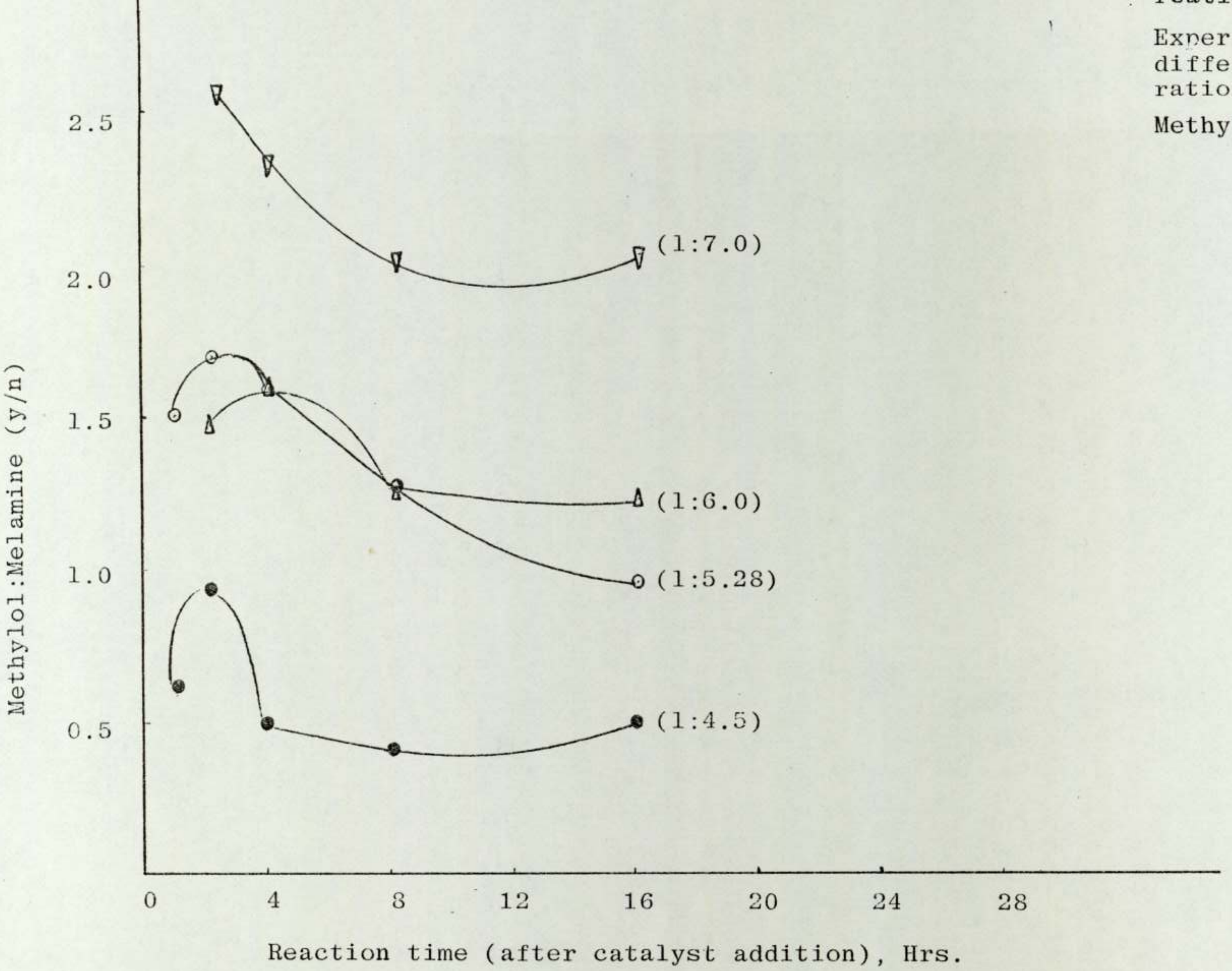
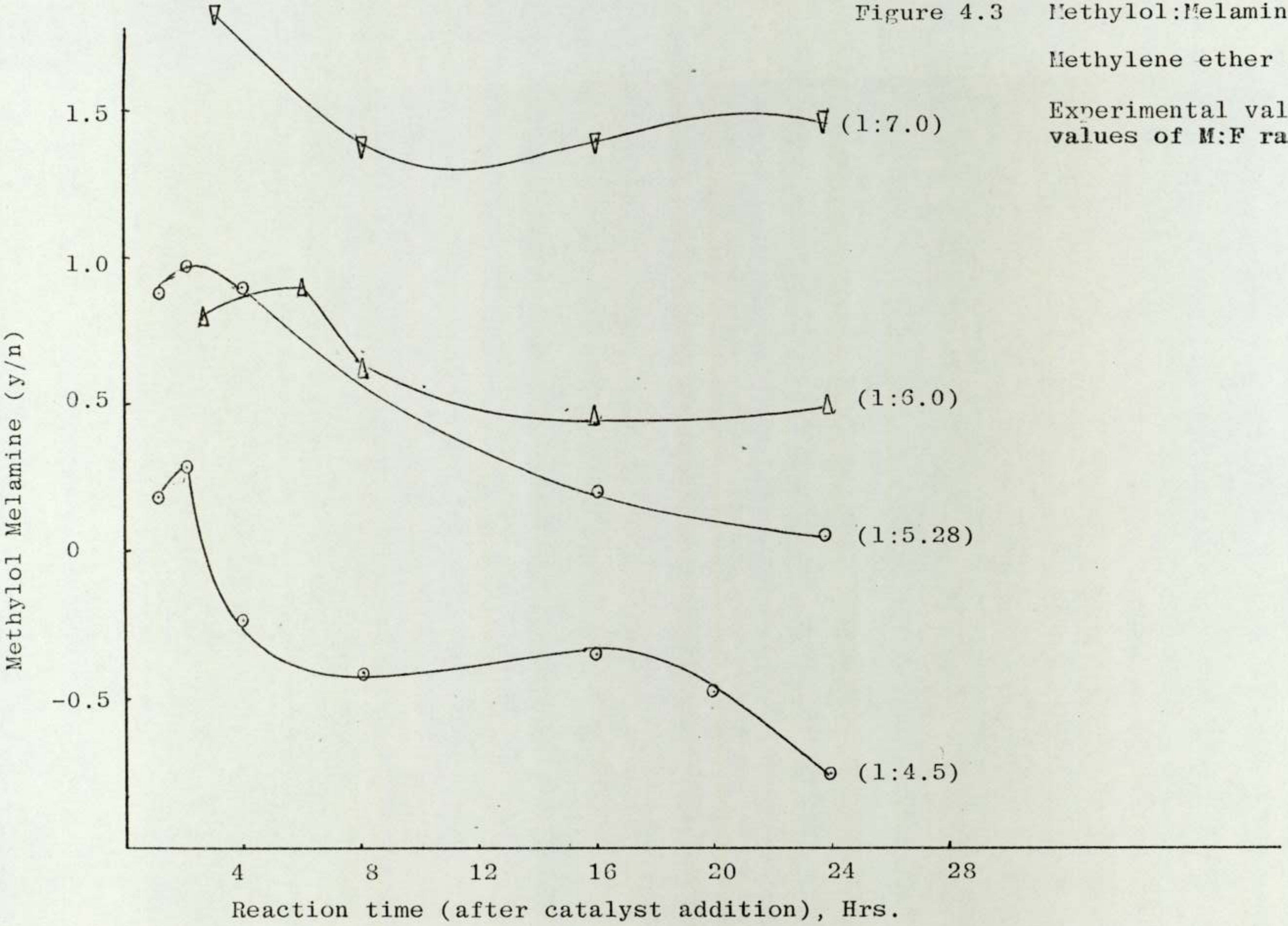


Figure 4.3 Methylol:Melamine vs reaction time

Methylene ether assumption.

Experimental values for different values of **M:F ratios.**



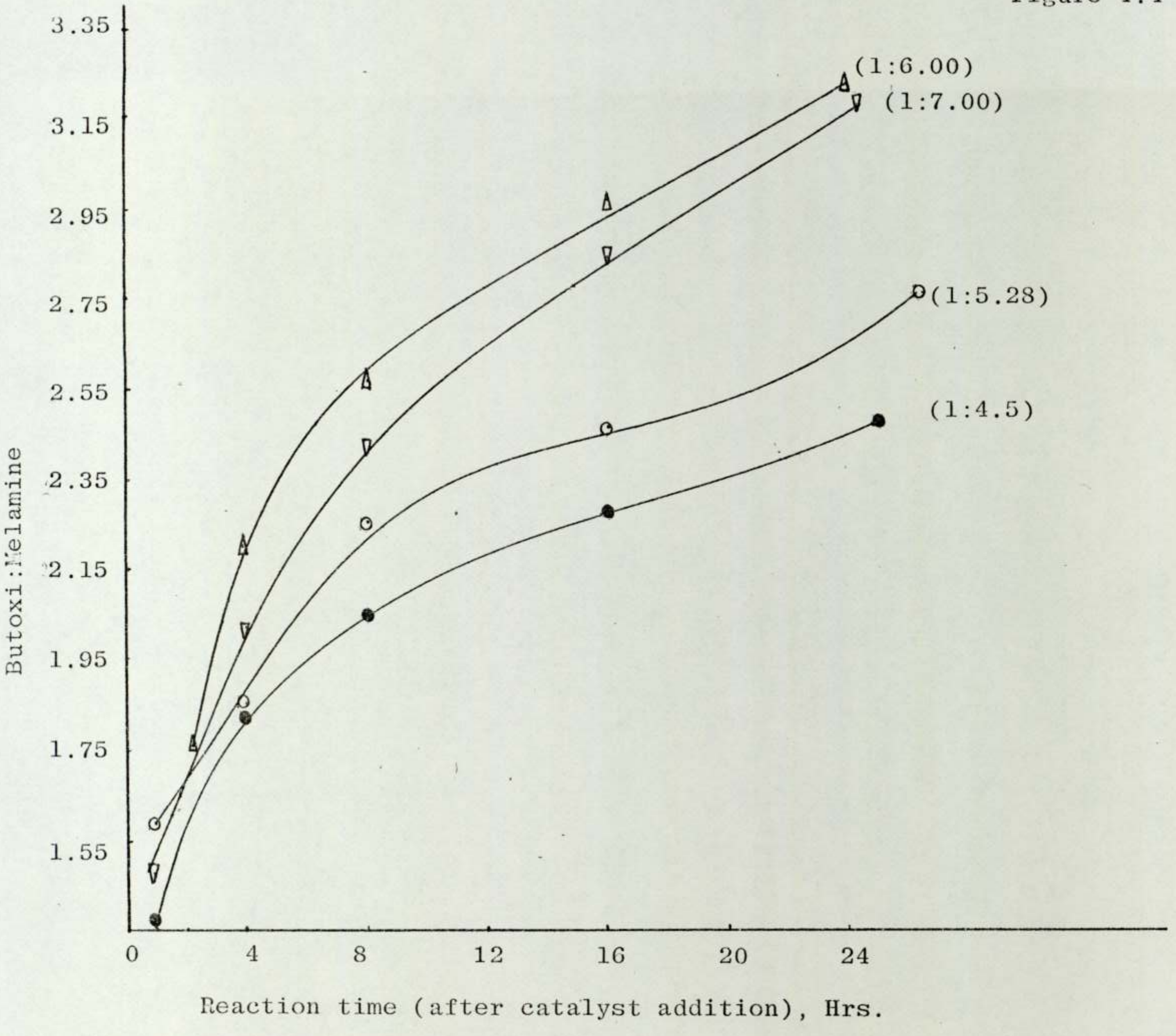


Figure 4.4 Butoxi:melamine vs reaction time

Experimental results.

Figure 4.5 White spirit tolerance vs reaction time
Experimental results for different
M:F ratios.

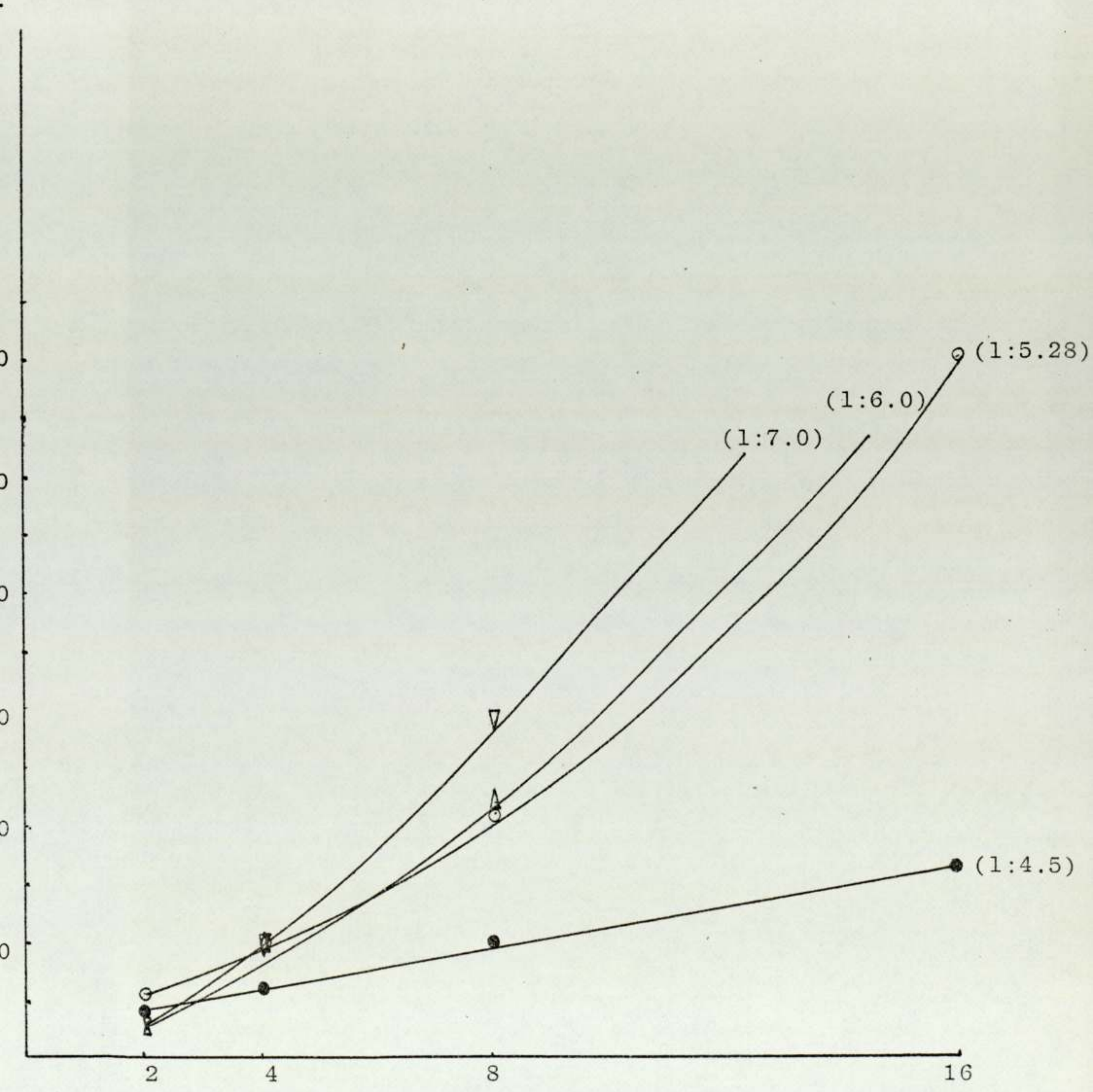
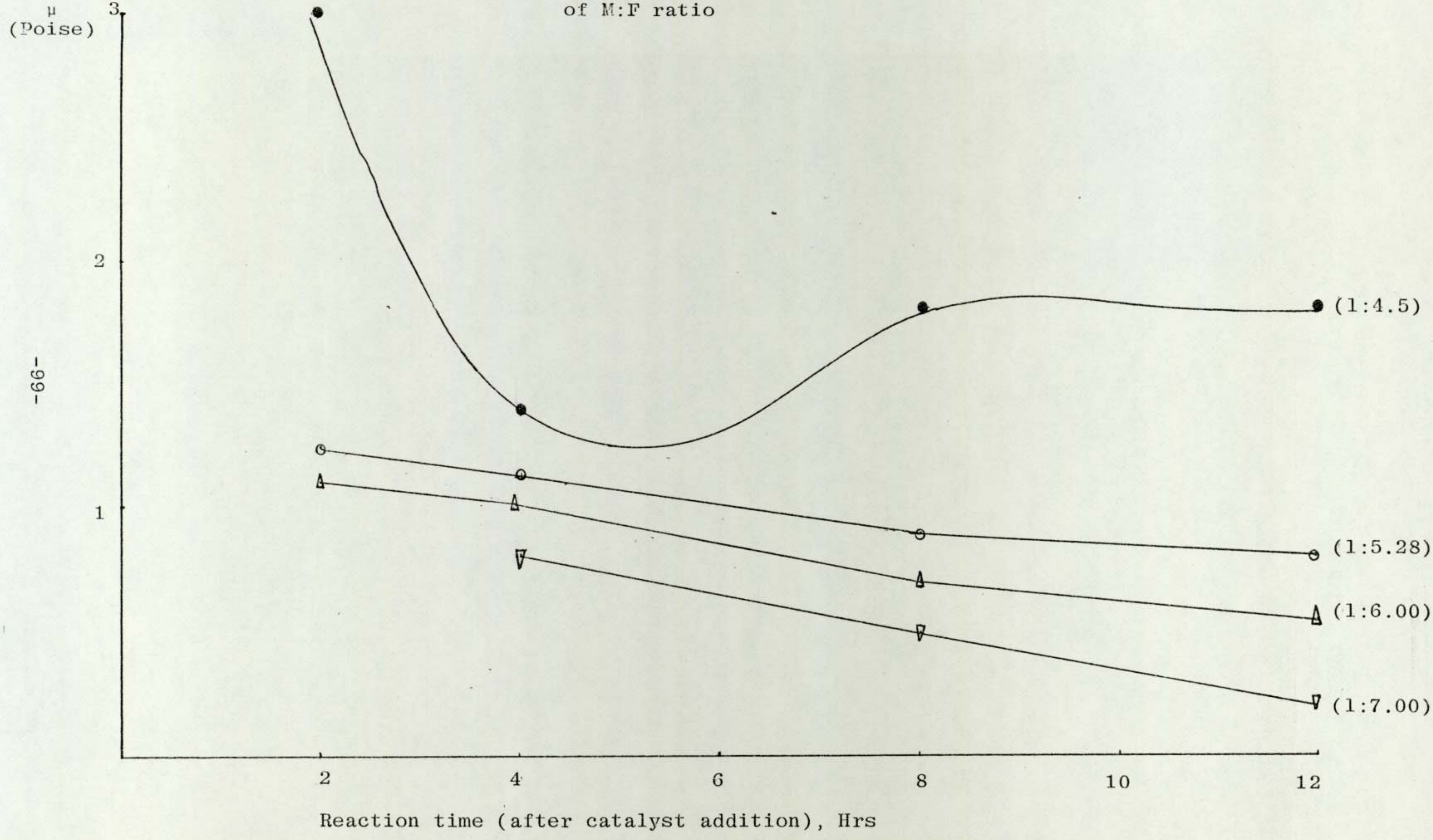


Figure 4.6 Viscosity vs reaction time

Experimental results for different values of M:F ratio



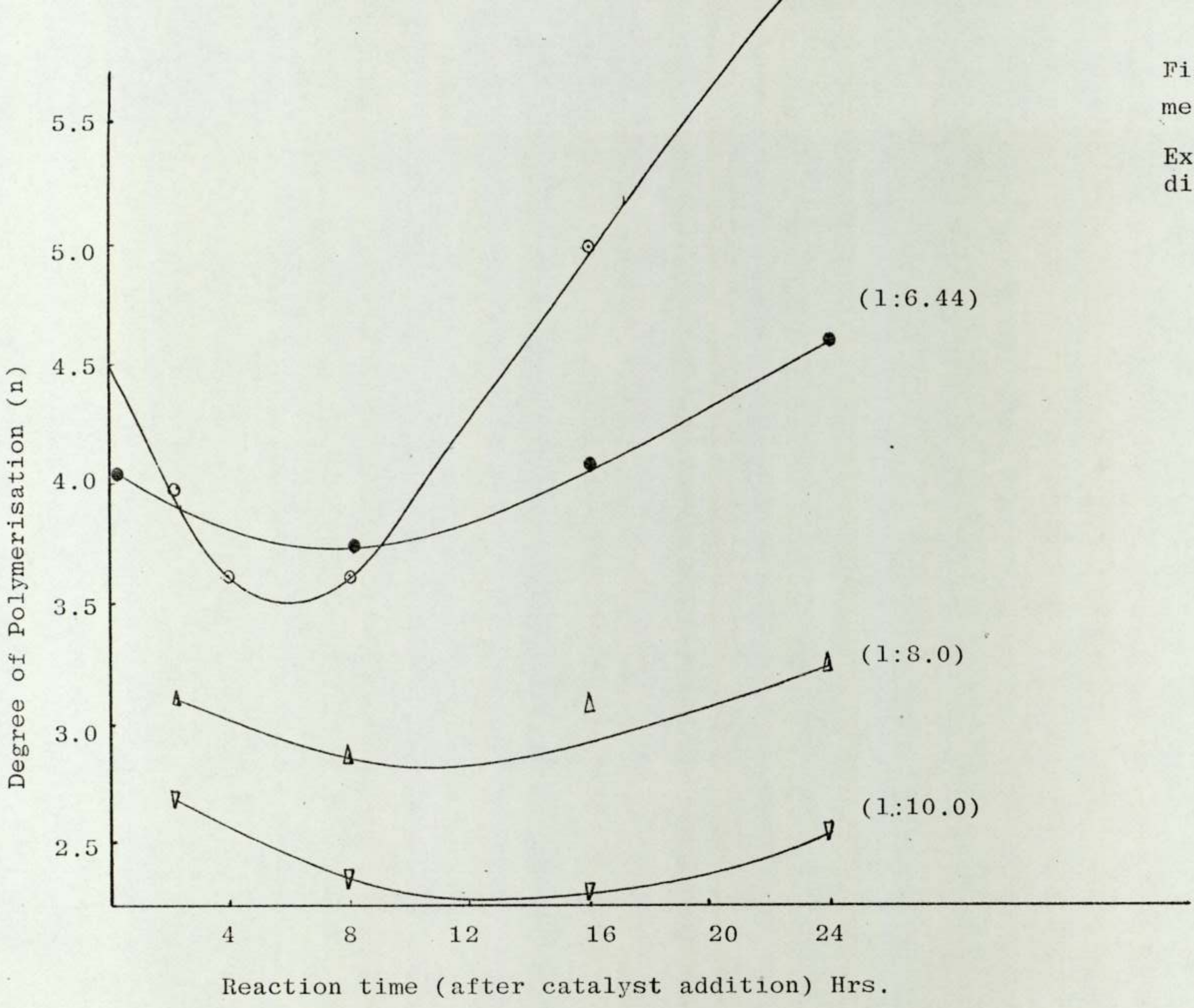


Figure 4.7 Degree of Polymerisation vs reaction time

Experimental values for different M:Bu ratios.

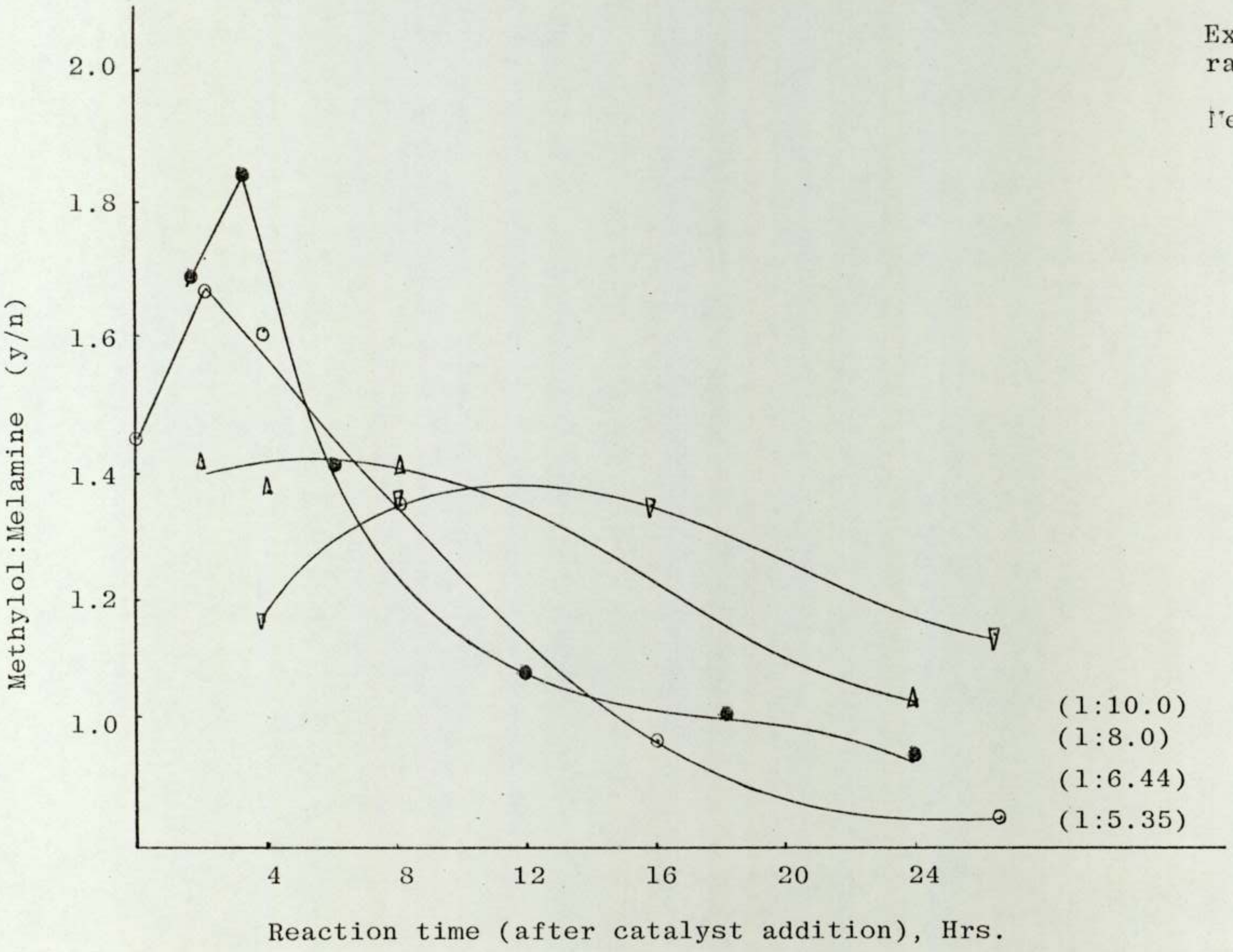


Figure 4.8 Methylol:Melamine vs Reaction time

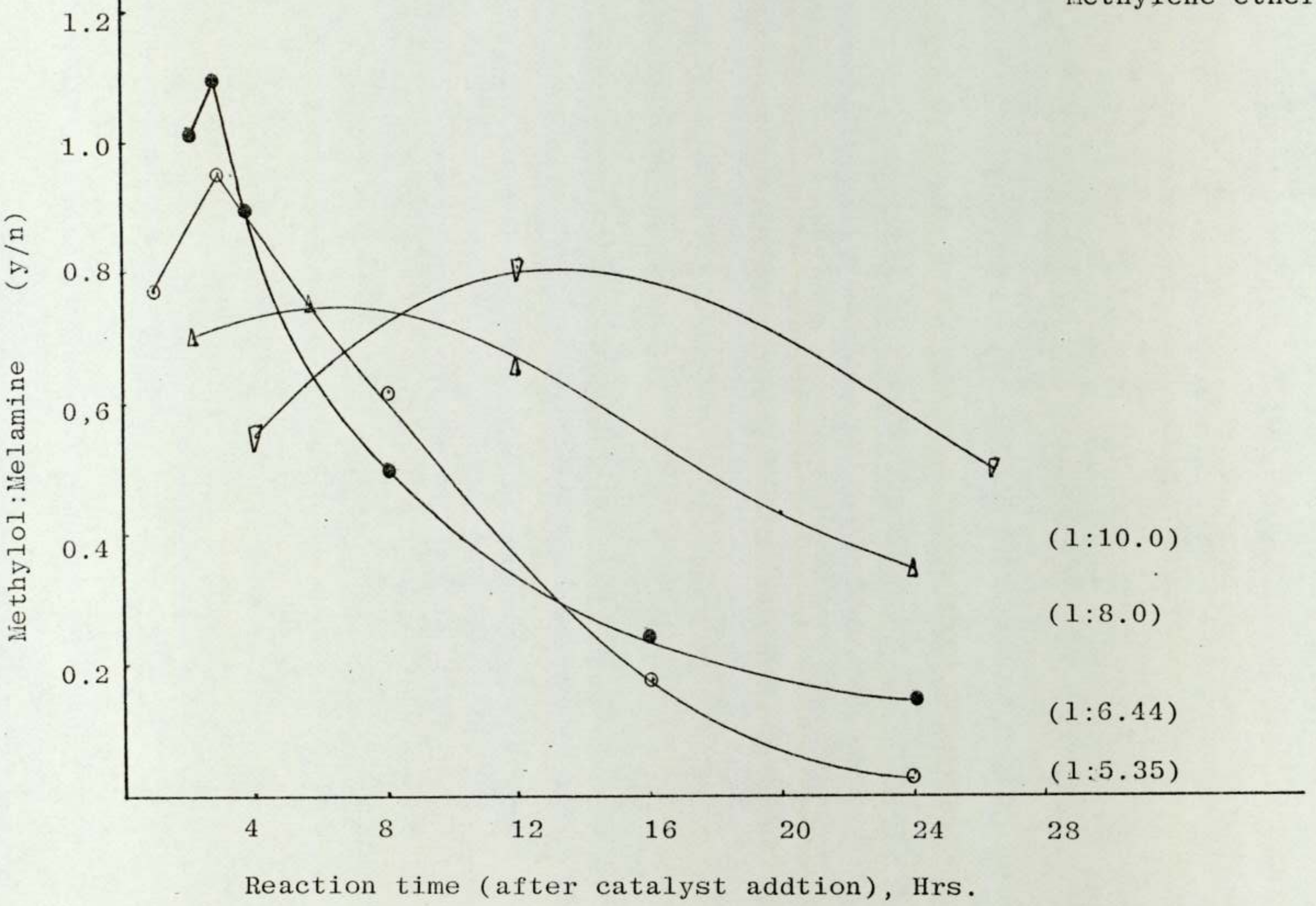
Experimental values of M:Bu ratios.

Methylene assumption.

Figure 4.9 Methylol:Melamine vs reaction time

Experimental values for different M:Bu ratios.

Methylene ether assumption.



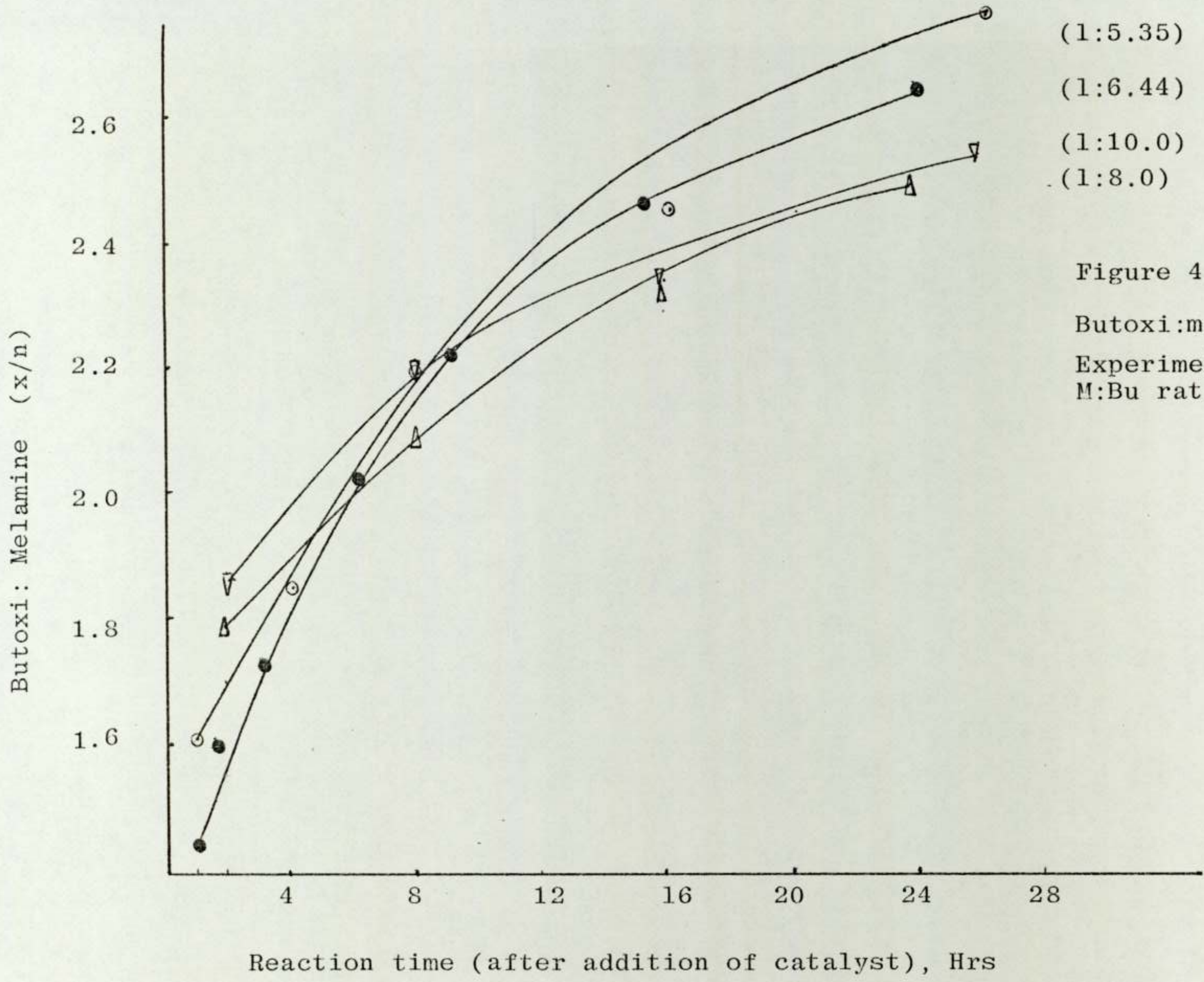


Figure 4.10

Butoxi:melamine vs reaction time

Experimental values for different
M:Bu ratios

Figure 4.11 White spirit tolerance vs reaction time

Experimental values for different M:Bu ratio.

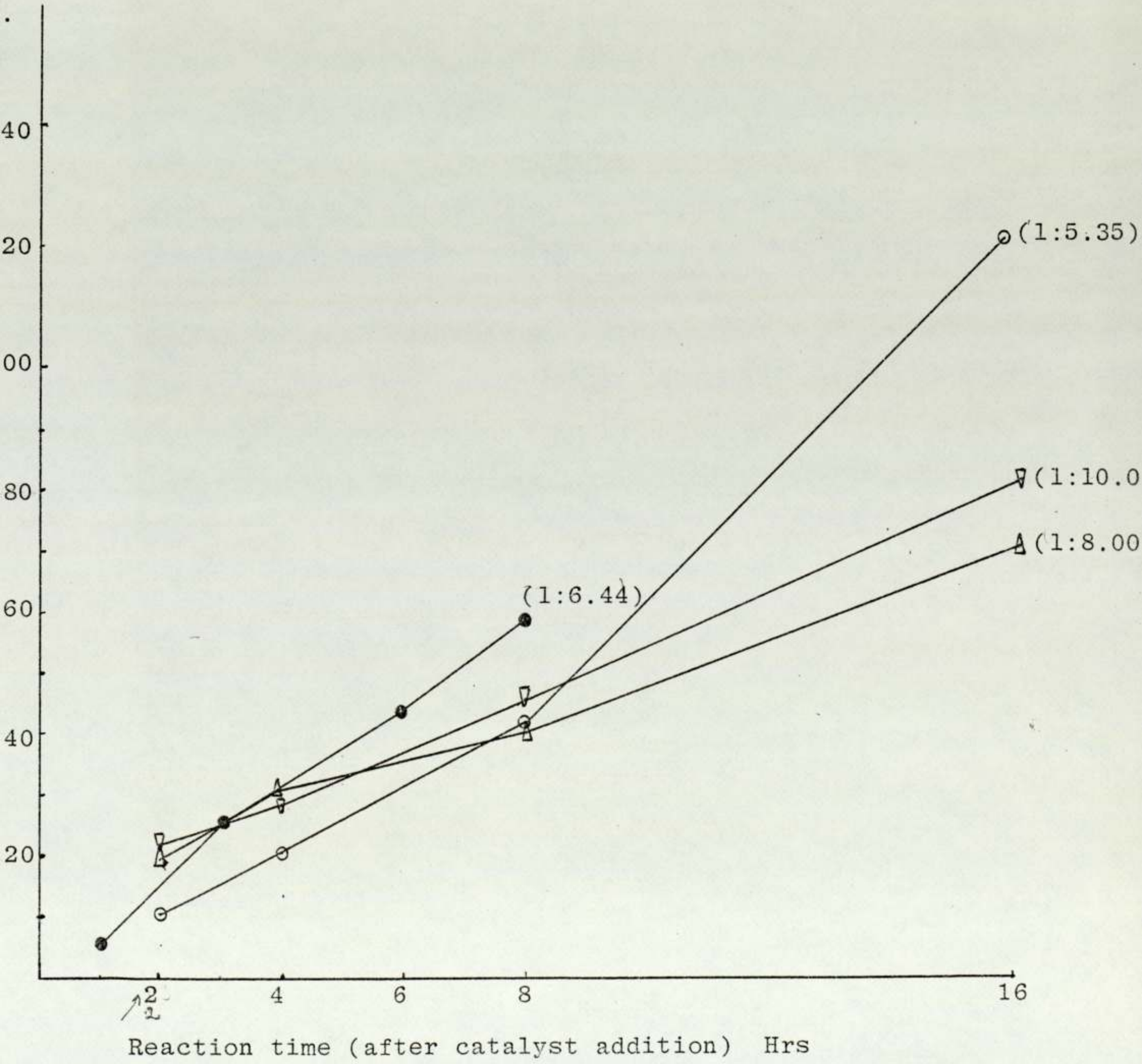
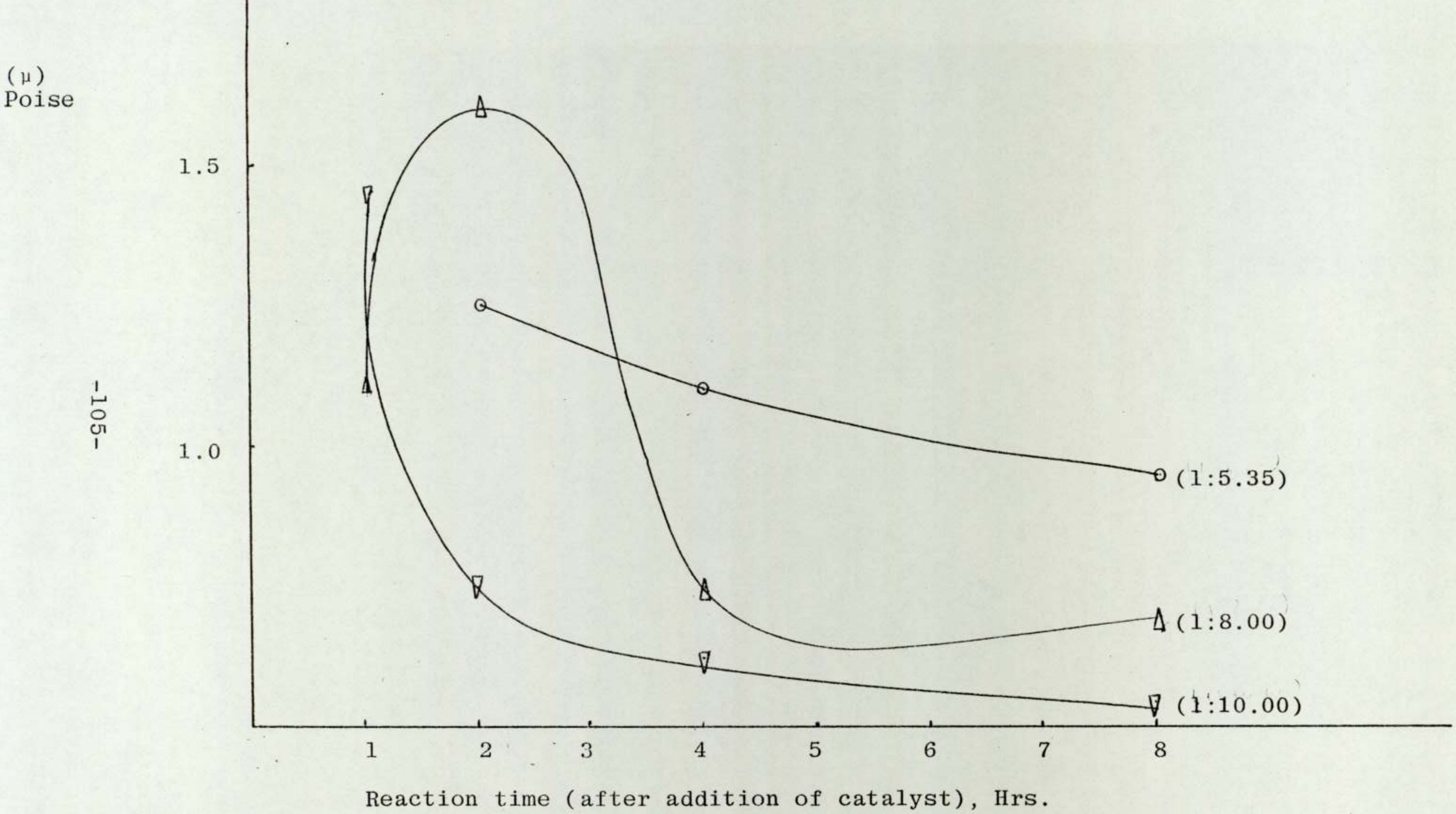


Figure 4.12 Viscosity vs reaction time

Experimental values for different M:Bu ratios



tolerance and therefore a resin well outside the specification. The trend of the curve is particularly sharp for the standard charge M:F = 1:5.28 and it can be explained by the reaction of methylene-ether bridges with butanol in acid conditions at the second stage of the process. In the literature different kinds of bridges in the structure of amino resins have been reported. As early as 1943, Gams and coworker (85) mentioned the possibility of two kinds of bridges resulting from two different condensation reactions. One bond, methylene bridge, resulting from the reaction of an amino group $-NH_2$ with a methylol group $R.\ CH_2OH$ yielding a methylene bridge ($RHN - CH_2 - NHR$) and a molecule of water, and a second type of linkage, methylene ether bridge resulting from the reaction of two methylol groups giving a methylene ether bridge ($RHNCH_2OCH_2NHR$) and water. This result was confirmed later by Kitagawa (100) and Wohnsiedler (104), who mentioned two other kinds of possible bonds arising from a ring closure reaction. The same results were obtained by Michaud (117) and Schedlbauer (89). Recent papers, using sophisticated analytical methods, could determine quantitatively the amount of different kinds of bridges present in the resin structure. This was the case of Kambanis (49) that using NMR spectrocopy and gel permeation chromatography, determined the proportion of the two kinds of bridges in urea-formaldehyde resins. He also confirmed that polymerisation under acid conditions proceeds via the formation of methylene bonds whereas under alkaline conditions dimethylene ether bridges were favoured. That is in accordance to the data of fig 4.1 since the first stage of reaction, not represented in the figure, occurs in mild alkaline conditions, therefore favouring the formation of dimethylene ether groups. After the acid addition the dimethylene ether bridges are broken and react with butanol causing a decrease in the degree of polymerisation. After some time of reaction the formation of methylene bridges balances the former reaction and an increase in the degree of polymerisation occurs again.

2. Contrary to fig 4.1 fig 4.2 shows an increase in methylol groups at the beginning of the second stage, and that increase is sharper for low M:F ratios. This lead us to the conclusion that the dimethylene ether bridges decomposition yields some methylol groups. It is interesting to notice that for M:F = 1:4.5 the methylol group concentration is low compared to the other cases, and that is a sign of high condensation reaction rate, therefore fast consumption of methylol groups.
3. In fig 4.4 it is clear that high melamine formaldehyde ratios favour the butylation reaction. For M:F = 1:4.5 the butylation reaction proceeds slowly when compared to higher ratios. For M:F = 1:6.0 or 7.0, the butylation reaction rates are similar and the fact that M:F = 1:6.0 shows higher values than M:F = 1:7 is not significant. It can be attributed to a concentration effect or lack of accuracy in the Zeiss method, used for the determination of butoxy-groups. For all

charges the reaction rate of butylation is higher in the first six hours of reaction.

4. In fig 4.5 it is shown how the resins tolerance to white spirit changes during the course of reaction. This property is known to be associated to the degree of butylation attained and is an indication of the balance between the two competing reactions at the second stage, condensation and butylation. As expected for all the ratios there is an increase of tolerance (compatibility) with time. However, the rate of change for low formaldehyde charges is extremely small when compared to the other cases. This is due to the high condensation rates that occurs when M:F = 1:4.5. Therefore, the balance between the two reactions is not right for low charges of formaldehyde and that makes the solvent compatibility value of the resin rather poor.
5. Fig 4.6 shows the variation of viscosity at constant oven solids, with reaction time. Again the behaviour of the curve for low melamine formaldehyde ratio is different from the other cases. There is a sharp decrease in the viscosity initially that is followed by a not so sharp increase in the viscosity. After 8 hours of reaction the values remain almost constant. For the other charges the figure shows a slow decrease in the values of the viscosity.
6. Fig 4.7; 4.8; 4.9; 4.10;4.11; 4.12 shows the results by A Firth for the experiments in which the melamine:formaldehyde ratio was kept constant and the melamine:butanol ratio varied. Fig4.7 reveals that the condensation rate is

slowed down by high charges of butanol. All the curves show a decrease in the degree of polymerisation in the beginning due to the reaction of the methylene ether bridges, but that is sharper for low melamine: butanol ratios. In this case the polymerisation recovers earlier and starts to increase at about 6 hours of reaction time. The overall trend is the same in fig 8 and 9 and they suggest that butanol acts like a tranquiliser, i.e, the reaction proceeds slowly in the presence of large quantities of butanol. The condensation reaction seems to be particularly affected by this effect. However, fig 4.10 shows there is also a decrease in the butylation ratio, that is not very pronounced, suggesting a concentration effect.

7. Fig 4.11 represents white spirit tolerance versus reaction time. It can be seen that the rate of charge of white spirit tolerance with time is higher for low melamine: butanol ratios. However, the values of white spirit tolerance in the first eight hours of the reaction are higher for higher melamine:butanol ratios. These results suggest that initially, when the butylation rate is still high, the resins with a high content of butanol in the reactor, show larger values of solvent tolerance. However, when butylation rates start to be slow for the high ratios of butanol, butylation is still proceeding at a reasonable rate for the case of melamine:butanol ratio of 1;5.28, making solvent tolerance rate of change higher in this case.

8. In fig 4.12 viscosity was plotted against reaction time. It is apparent that viscosity decreases with reaction

time and that high amounts of butanol leads to a resin of lower viscosity. The values for melamine:butanol ratio of 1:6.44 were so low that could not be represented in the figure.

Having discussed the results from Firth's work and studied the influence of varying the proportion of the reactants in the charge, a kinetic model was developed to simulate the reactions involved in the manufacture of butylated formaldehyde-melamine resins.

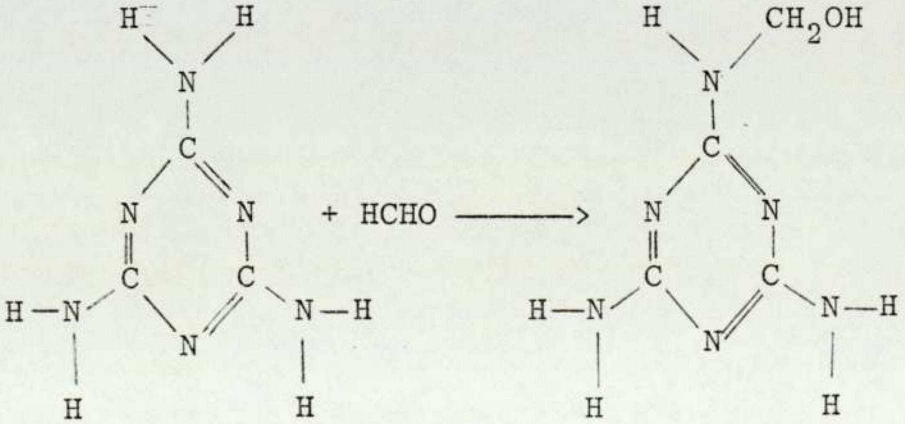
## 4.3 Description of the Model

As was mentioned before, the manufacture of butylated formaldehyde melamine resins can be divided in several stages, two of which are the focus of our attention. As a consequence of the natural division of the process into stages the mathematical model also has two distinct stages. The data just presented in previous sections refers to the second stage of the model, after the catalyst addition. No information about the 1st stage of the process is available. In this period the water is being extracted and the reactions mixture consist of an heterogeneous solution which is difficult to analyse by conventional analytical methods.

### 4.3.1 First Stage Model

The reactions considered to be taking place in the first stage of the process are:-

Methylolation: Formation of methylol groups in the ring structure of melamine by reaction of the amino groups ($(NH_2)$) of the melamine molecule with formaldehyde.



The reaction scheme, represented on the previous page, illustrates the formation of mono-methylol melamine. The methylolation reaction involves the formation of all the possible methylol derivatives of melamine that are known to be formed. There are nine possible forms of methylolmelamine, from mono to hexamethylolmelamine, having di-tri and tetramethylolmelamine two possible isomeres. This reaction has been the topic of study of many papers (see chapter 2) and is a second order reaction being the rate equation given by: Rate of methylation = $R_m = K[HCHO][-H]$

It has been mentioned in the literature [85] that the ability of the hydrogen in the amino group to react with formaldehyde is different according to if the amino group is already mono-substituted or not. That is, the reactivity of the group - $NHCH_2O$ is small compared to the reactivity of the amino group on its own - $NH_2$. Due to this factor the rate of methylolation tends to decrease as the concentration of methylol groups increase, i.e, as the amount of formaldehyde reacted increases. Another factor that also contributes for decrease in the rate of methylolation is what is called the stereo effect [19]. This effect is related to the size of the molecules taking part in the reaction. As the resin manufacture progresses and the polymerisation proceeds the average size of the molecules in the reaction grow due to the formation of dimers, trimers etc, polymers with the basic ring structure. These are big molecules with many functional groups in a compact form. Its form is not very prone to reaction with other molecules because of lack of space near the reactive points, i.e, the collision of the molecules of the functional groups reacting becomes less probable. From the data, on which the model is based it was noticed a decrease in the rate of methylolation specially in the end of the second stage. Therefore a parameter S was defined that takes into consideration the two factors just described.

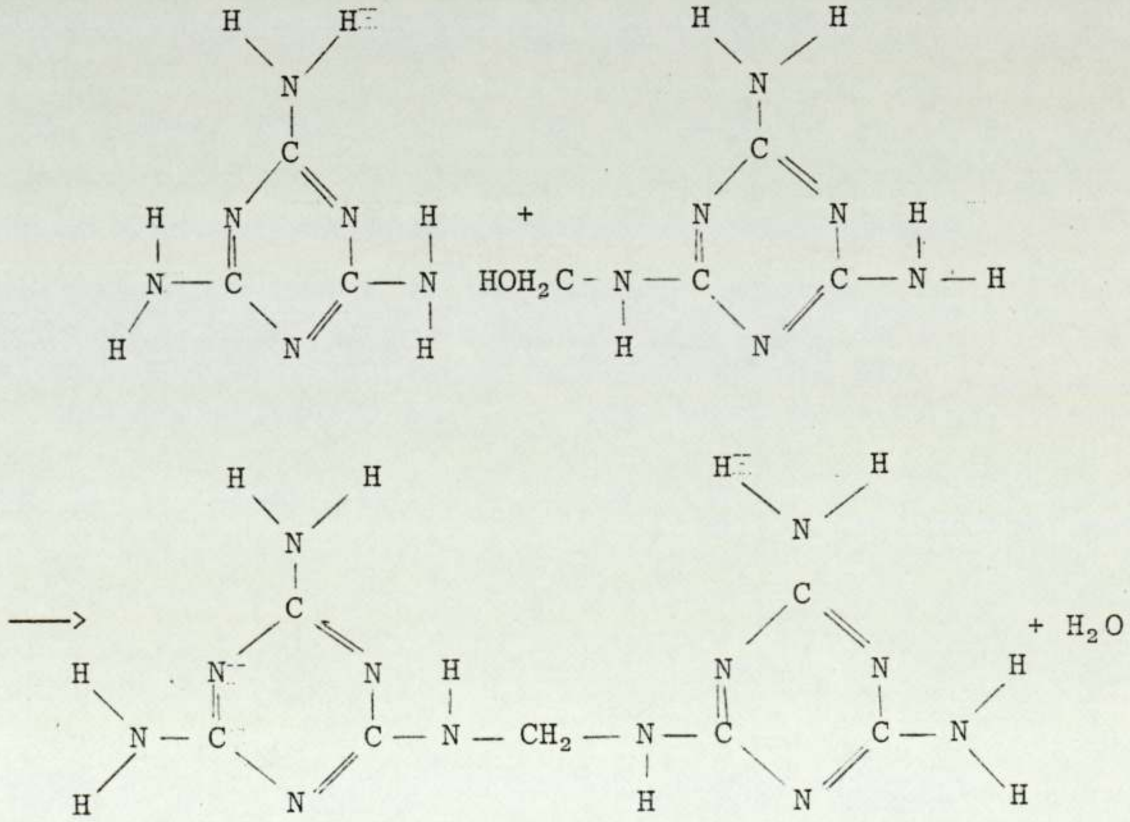
S was described the equation

$$S = \% \text{ of formaldehyde reacted x} \sqrt{\text{molecular weight}}$$

The transition value for which the methylolation rate decreases sharply was determinedto be 28. Therefore, this parameter is going to appear in the simulation program and the methylolation rate constant will decrease sharply when S reaches the value 28.

Condensation reactions:

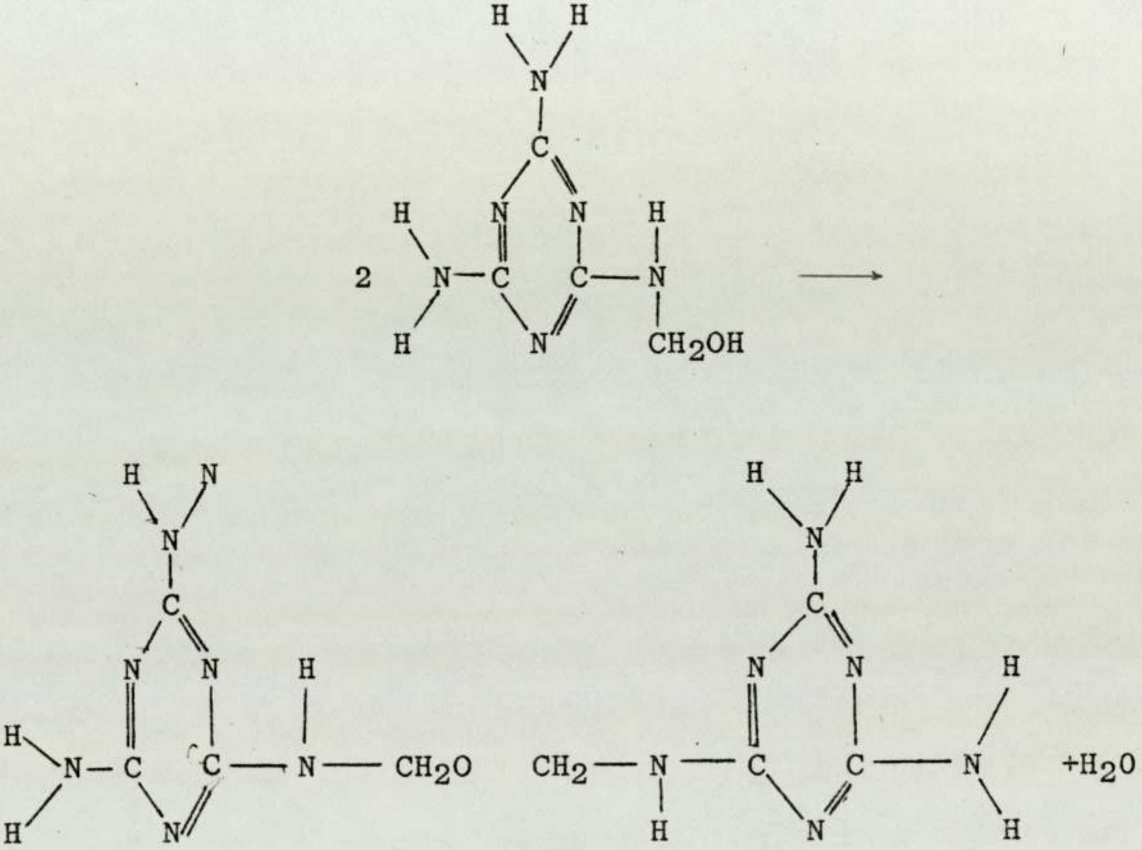
1. Formation of methylene bridge by reaction of a methylol group with an amino group



This reaction is a second order reaction, as it has been reported in the literature, Kitagawa (100), and the rate equation can be represented by:

Rate of methylene bridge formation = $R_c = K_1(-H)(-CH_2OH)$.

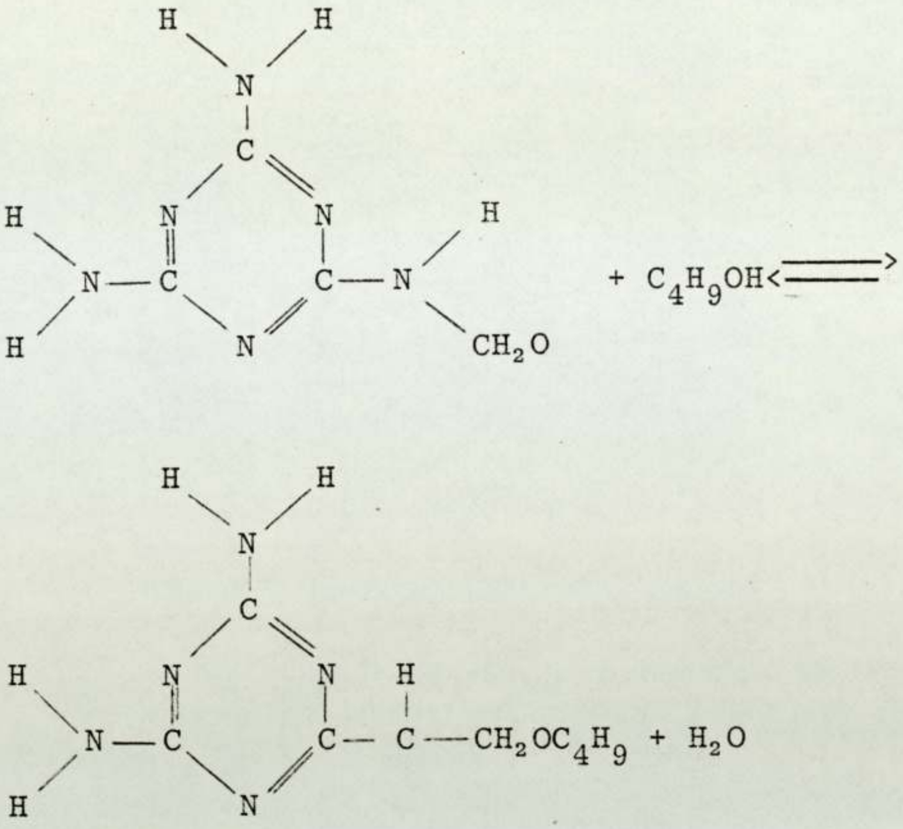
2. Formation of methylene ether bridge by reaction of two methylol groups



This reaction is a second order reaction, and the rate equation can be represented by:

Rate of methylene ether bridge formation = $R_c = K_5 (-CH_2OH)^2$.

In parallel with the two condensation reactions the butylation reaction is also considered. It consists of the reaction of a methylol group with butanol with for formation of a butoxi group.



This reaction was considered reversible andfirst order relatively to the methylol group concentration. The butanol concentration does not appear in the rate equation. The fact that butanol concentration has no influence in the rate equation was reported by Schedlbauer in his work on butylated formaldehyde melamine resins and was confirmed by the data of BIP, specifically in fig 4.10 of section 4.2.2. The rate equation is,

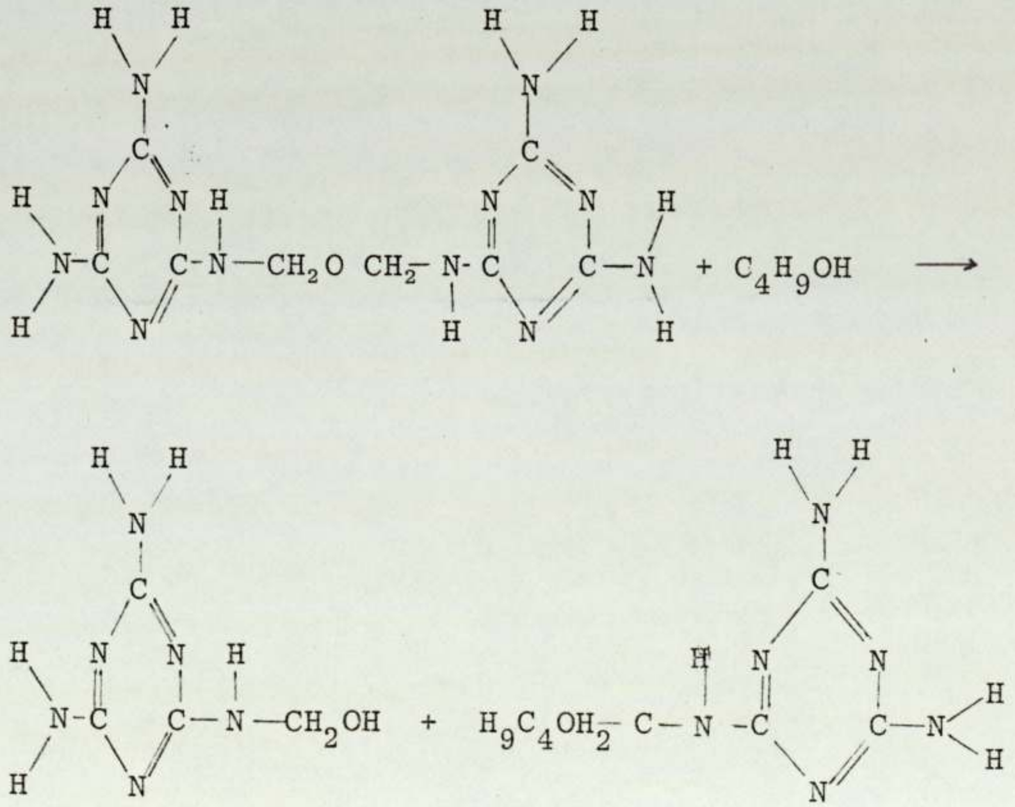
rate of formation of butoxy groups = $R_b = K_2$ $[-CH_2OH]$ (butylation)

rate of the inverse reaction = $R_{b_1} = K_3[-CH_2OC_4H_9]$ $[H_2O]$

The inverse reaction of butylation is represented by a second order rate equation, due to the fact, several times mentioned in the literature, of water having an unfavourable effect on the butylation reaction. That is one ofthe reasons of the extraction of the water from the reactor in the first stage of the process. The acid catalyst is added only when the water introduced in the reactor when formalin was charged, has been completely removed.

### 4.3.2 Second Stage Model

The reactions considered in the second stage of the process differ from the first stage in the reaction involving the methylene-ether bridge formation. It is known that when the pH of the medium is lowered the condensation proceeds via the methylene bridge formation [49]. Therefore, in acidic medium no methylene-ether bridges are being formed, but contrarily they are reacting and yielding back butoxi and methylol groups, according to the reaction scheme:



This reaction is a first order in relation with the methylol-ether bridge concentration and the rate equation is given by

$$R_H = K_4\ [-CH_2OCH_2-]$$

### 4.3.3 Assumptions used in the Simulation Model

1. The water removal rate was determined according to some typical results of B.I.P. The water removal rates obtained in the pilot plant at Aston University were not exactly the same, but the differences were not substantial.
2. The water removal rate was considered to vary linearly inbetween the sample points, i.e, the water removal rates were calculated by linear interpolation for the points inside the internal of two measurements.
3. Temperatures of the reactor was considered constant. It is known that variations in the temperature of the reactor are not significant during the course of reaction. The temperature changes in the reactor during a batch are smaller than 15°C.
4. No loss of butanol was considered. It is known that a small amount of butanol is dissolved in the water that is removed in the process. However, this amount is negligible when compared with the amount of butanol in the initial charge.
5. Methanol has no influence in the course of reaction. In order to stablise the formalin, and prevent formaldehyde precipitating about 7% in weight of methanol is added to the solution. This methanol is formed in the separator equally distributed in the

two phases and its content in the reactor decreases gradually as it is removed with the water of the process [117].

6. Cannizzaro reaction was considered negligible. The methylolation of melamine in alkaline conditions is accompanied, as a side reaction, by the Cannizzaro reaction, i.e, disprotonation of formaldehyde to yield formic acid and methylol, according to

   $$2HCHO + H_2O \longrightarrow HCOOH + CH_3OH$$

   According to studies by Lapina [76], this reaction only proceeds signficantly for pH above 9, much higher than the pH used in the pilot plant reactor.
7. Based on the data from BIP for the standard charge M:F:B = 1:5.28:5.35, and the decrease in degree of polymerization in the early states of the second stage it was assumed that at the end of the first stage the amount of methylene ether bridges was 28% of the total amount of bridges (sec 4.3.7)
8. No loss of formaldehyde was considered during the process. In the initial stages of the process it is common for some haziness to appear in the separator. This is normally attributed to some formaldehyde that was distilled together with butanol and water. This effect is not important, as the haziness only persists a short time and disappears before the xylol addition. The amount of formaldehyde lost is therefore negligible.

### 4.3.4 Mathematical Formulation of the Simulation Model

According to section 4.3.1, the simulation model for the first stage of the process takes the following form:

$$\frac{d[-CH_2-]}{dt} = K_1\ [-H][-CH_2OH]$$

$$\frac{d[-CH_2OC_4H_9]}{dt} = K_2\ [-CH_2OH] - K_3\ [-CH_2OC_4H_9]\ [H_2O]$$

$$\frac{d[C_4H_9OH]}{dt} = -K_2\ [-CH_2OH] + K_3\ [-CH_2OC_4H_9]\ [H_2O]$$

$$\frac{d[H_2O]}{dt} = K_1\ [-H]\ [-CH_2OH] + K_2\ [-CH_2OH] - K_3$$

$$[-CH_2OC_4H_9]\ [H_2O] + K_5V\ [-CH_2OH]^2 - \frac{R}{V} * (1000/18)$$

$$\frac{d[-H]}{dt} = -K\ [HCHO]\ [-H] - K_1\ [-CH_2OH]\ [-H]$$

$$\frac{d[-CH_2OH]}{dt} = K\ [HCHO]\ [-H] - K_1\ [-CH_2OH]\ [-H] -$$

$$- 2 \times K_5\ [-CH_2OH]^2 - K_2\ [-CH_2OH] + K_3\ [-CH_2OC_4H_9]$$

$$[H_2O]$$

$$\frac{d[-CH_2OCH_2-]}{dt} = K_5\ [-CH_2OH]^2$$

$$\frac{d[HCHO]}{dt} = -K\ [-H]\ [HCHO]$$

$$\frac{dV}{dt} = -R$$

The water removal rate was calculated according to table 4.3.In the pilot plant process the melamine charge is 12.6 kg. Therefore, the water distillation rate was scaled down by the appropriate factor 1075/12.6. The values obtained are shown in table 4.3

| TIME (HOURS) (AFTER XYLOL ADD) | WATER DISTILLATION RATE (LITRES/h) | RATE IN LITRES/MINUTE |
|---|---|---|
| 0 | 0 | 0 |
| 1 | 4.16 | 0.069 |
| 2 | 8.50 | 0.142 |
| 3 | 6.56 | 0.109 |
| 4 | 4.69 | 0.078 |
| 5 | 2.81 | 0.047 |
| END OF 1ST STAGE | ACID ADDITION | |

Table 4.3 - values of the water removal rate for the 1st stage of reaction

As the volume is changing during the reaction the model equations were rewritten in terms of number of moles instead of concentrations inthe simulation program.

For the second stage model and according to the chemical reactions used in section 4.3.2, the following equations were used:

$$\frac{d[-CH_2-]}{dt} = K_1\ [-CH_2OH]\ [-H]$$

$$\frac{d[-CH_2OC_4H_9]}{dt} = K_2\ [-CH_2OH-]\ -K_3\ [-CH_2OC_4H_9]\ [H_2O] + $$

$$+ K_4\ [-CH_2OCH_2-]$$

$$\frac{d[C_4H_9OH]}{dt} = -K_2\ [-CH_2OH] + K_3\ [-CH_2OC_4H_9]\ [H_2O] -$$

$$- K_4\ [-CH_2OCH_2-]$$

$$\frac{d[H_2O]}{dt} = -R \times (1000/18)/V + K1\,[-CH_2OH]\,[-H] + K2\,[-CH_2OH] - K3\,[-CH_2OC_4H_9]\,[H_2O]$$

$$\frac{d[-H]}{dt} = -K \times [HCHO]\,[-H] - K1 \times [-CH_2OH]\,[-H]$$

$$\frac{d[-CH_2OH]}{dt} = K \times [HCHO]\,[-H] - K1 \times [-CH_2OH]\,[-H] - - K2\,[-CH_2OH] + K3 \times [-CH_2OC_4H_9] + K4\,[-CH_2OCH_2-]$$

$$\frac{d[-CH_2OCH_2-]}{dt} = -K4 \times [-CH_2OCH_2-]$$

$$\frac{d[HCHO]}{dt} = K \times [HCHO]\,[-H]$$

$$\frac{dv}{dt} = -R$$

## 4.3 Program and Symbols

For the integration of the set of ordinary differential equations the Aston Simulation Package was used. A brief description of the subroutines used follows:

| Subroutine | Main Program | Observations |
|---|---|---|
| 1 | CALL (1, T) | Initialises "housekeeping variables and sets T (the independant variables) to zero. |
| 2 | CALL (2, P, E, F1, F2) | Sets F1 = 2 if T = E, where E is the final value of T (i.e, end of a run) otherwise F1 = 1.<br>Sets F2 = 2 if T = 0 or a value at which output is required otherwise F2 = 1. |

| | | |
|---|---|---|
| 3 | CALL (3, T, S, I) | Updates the value of T and selects the integration procedure. S = step length. I = 2 modified Euler method is used. I = 4 Runge Kutta fourth order method is used. |
| 4 | CALL (4, $Y_1$, D1) | Integrates D1 (i.e, dy/dt) to give Y1. Subroutine 4 will be called as many times as the number of first order derivatives in the problem description, |

Symbols used in the program.

| | |
|---|---|
| F | Number of moles of formaldehyde |
| H1 | Number of moles of hydrogen in the amino groups |
| M2 | Number of moles of methylol groups |
| M1 | Number of moles of methylene bridge |
| M3 | Number of moles of methylene ether bridges |
| Bo | Number of moles of butanol |
| B1 | Number of moles of butoxy groups |
| W1 | Number of moles of water |
| V | Volume of the mixture in the reactor |
| K | Rate constant of methylolation reaction |
| $K_1$ | Rate constant of condensation (formation of methylene bridges) |
| $K_2$ | Rate of constant of butylation |
| $K_3$ | Rate constant of the inverse reaction of butylation |
| $K_4$ | Rate constant of the reaction between methylene ether bridges and butanol |

| | |
|---|---|
| K5 | Rate constant of condensation (formation of methylene-ether bridges) |
| F3 | Formaldehyde reacted per mole of melamine |
| B2 | Number of butoxi groups per mole of melamine |
| N | Degree of polymerisation (number of bridges per unit of melamine) |
| M4 | Molecular weight of the resin |
| S1 | Parameter of methylolation reaction |
| A(I) | Vector containing the water removal rates for the second stage of reaction |
| B(I) | Vector containing the water removal rates for the first stage of reaction |
| R | Water removal rate |

### 4.3.6 Initial Values of the Program

According to the values used in the laboratory (Table 1 - Section 3.1.2) the pilot plant values for the initial change were calculated using a factor of 5.0, that is the ratio between the capacity of the reactor in the pilot plant and the reactor in the laboratory (table 4.4).

```
ST

   DIM A(8),B(6)
   FOR J=1 TO 6
   READ B(J)
   NEXT J
   DATA 0,.69E-01,.142,.109,.78E-01,.47E-01
   P=30:E=270
   I=4:S=6
   CALL (1,T)
   REM    INITIAL CONDITIONS
   F=523:H1=600:M2=0
   B2=0:F3=0:N=0:M4=0:S1=0
   M1=0:M3=0
10  K=.105E-02
5   K1=.46E-03
0   K2=.64E-02
5   K3=.25E-03
20  K5=.45E-03
30  W1=1538.9:V=39.2
0   B0=450:B1=0
50  REM    DERIVATIVES
53  GOSUB 1500
55  D0=-R
0   D1=K1*M2*H1/V
5   D2=K2*M2-K3*B1*W1/V
70  D3=-K2*M2+K3*B1*W1/V
80  D4=K1*M2*H1/V+K2*M2-K3*B1*W1/V+K5*M2↑2/V-R*1000/18
90  D5=-K*F*H1/V-K1*M2*H1/V
92  D6=K*F*H1/V-K1*M2*H1/V-2*K5*M2↑2/V-K2*M2+K3*B1*W1/V
94  D7=K5*M2↑2/V
96  D8=-K*H1*F/V
    REM    TEST FOR OUTPUT AND END
    CALL (2,P,E,F1,F2)
10  IF F2=1 THEN  GOTO 250
20  IF T=180 THEN B0=B0+90
25  IF T=180 THEN V=V+8.2
30  PRINT
32  PRINT
35  PRINT T,M1,M2,M3,H1
37  PRINT
40  PRINT B1,B0,W1,R,V
42  PRINT
44  PRINT B2,F3,N,M4,S1
50  IF F1=2 GOTO 460
60  REM    INTEGRATION
70  CALL (3,T,S,I)
80  CALL (4,V,D0)
90  CALL (4,M1,D1)
00  CALL (4,B1,D2)
10  CALL (4,B0,D3)
20  CALL (4,W1,D4)
30  CALL (4,H1,D5)
40  CALL (4,M2,D6)
50  CALL (4,M3,D7)
60  CALL (4,F,D8)
65  B2=B1/100
70  F3=(M1+2*M3+B1+M2)/100
80  N=100/(100-M1-M3)
```

```
0  S1=100*F3/528*SGR(M4)
0  IF S1>28 THEN K=.25E-03
5  GOTO 153
0  FOR J=1 TO 6
0  READ A(J)
0  NEXT J
0  DATA .43E-01,.24E-01,.11E-01,.5E-02,.3E-02,.2E-02
5  A(7)=0:A(8)=0
00  P=60:E=480
0  I=4:S=6
20  CALL (1,T)
30  K=.13E-02
40  K1=.1E-03
50  K2=.155E-02
60  K3=.1E-03
0  K4=.29E-02
80  REM      INITIAL CONDITIONS
0  REM      DERIVATIVE SECTION
20  GOSUB 2050
30  D0=-R
40  D1=K1*M2*H1/V
50  D2=K2*M2-K3*B1*W1/V+K4*M3
0  D3=-K2*M2+K3*B1*W1/V-K4*M3
70  D4=-R*1000/18+K1*M2*H1/V+K2*M2-K3*B1*W1/V
80  D5=-K*F*H1/V-K1*M2*H1/V
90  D6=K*F*H1/V-K1*M2*H1/V-K2*M2+K3*B1*W1/V+K4*M3
00  D7=-K4*M3
10  D8=-K*F*H1/V
20  CALL (2,F,E,F1,F2)
30  IF F2=1 GOTO 790
40  PRINT
50  PRINT
60  PRINT T,M1,M2,M3,H1
70  PRINT
80  PRINT B1,B0,W1,F,V
80  PRINT
84  PRINT B2,F3,N,M4,S1
90  IF F1=2 GOTO 970
00  CALL (3,T,S,I)
10  CALL (4,V,D0)
20  CALL (4,M1,D1)
30  CALL (4,B1,D2)
40  CALL (4,B0,D3)
50  CALL (4,W1,D4)
60  CALL (4,H1,D5)
70  CALL (4,M2,D6)
80  CALL (4,M3,D7)
90  CALL (4,F,D8)
00  B2=B1/100
10  F3=(M1+2*M3+B1+M2)/100
20  N=100/(100-M1-M3)
30  M4=108*N*(1+.518*B2+.278*F3)+18
40  S1=100*F3/528*SGR(M4)
50  IF S1>28 THEN K=.25E-03
60  GOTO 620
70  END
500  T1=T/60+1
510  T2=INT(T1)
530  R=F(T2)+(F(T2+1)-F(T2))*(T1-T2)
540  RETURN
050  T1=T/60+1
060  T2=INT(T1)
070  IF T1>=6 GOTO 2100
080  R=A(T2)+(A(T2+1)-A(T2))*(T1-T2)
090  RETURN
100  R=A(6)
2110  RETURN
120  END
```

| Reactants | Molecular Weight (g) | Molar Ratio | Charge | No of moles | No of moles of funct. groups |
|---|---|---|---|---|---|
| Melamine | 126 | 1 | 12.6 kg | 100 | (-H) 600 |
| Formaldehyde | 30 | 5.28 | 15.8 kg | 528 | (HCHO) 528 |
| Formalin 36.4% w/w | | | 43.5 kg | | |
| Water | 18 | | 27.7 kg | 1538.9 | |
| Butanol (1) | 74 | 4.5 | 33.3 kg | 450 | |
| Butanol (2) | 74 | 0.9 | 6.6 kg | 90 | |
| Xylol | 106 | $48 cm^3$/mole m | 4.8 l | | |
| Acid | | 2.8 $cm^3$/mol m | .28 l | | |

Table 4.4 - No of moles of each chemical specie in the pilot plant reactor.

Considering the density of formaldehyde as 1.02 and butanol as 0.81 the initial volume of the reactors charge was calculated:

$V_i$ = formalin + butanol + xylol = 43.3 + 41.1 + + 4.8 = 89.2

### 4.3.7 Tuning of the Model

In order to calculate the values of the kinetic constants the following sequence of calculations was done:

1. The conditions at the end of the first stage of the process were calculated from Firth's data for the standard charge M:F:Bu = 1:5.28:5.4.

   $$\text{Butoxi number} = \frac{\text{no moles butoxi group}}{\text{no moles melamine}} = 1.5$$

   $\therefore$ no moles butoxi group = 1.50

   no moles butanol in the reactor = Initial no of moles of butanol - 150 = 390

   degree of polymerisation = 4.5 = Average number of melamine units that constitute the polymer

   $\therefore$ no moles of the polymer = 100/4.5

   As there are (n-1) bridges per polymer unit the no moles of bridges = (100/4.5) x 3.5 = 77.8

   $$\text{In general no moles of bridges} = \frac{100(n-1)}{n} =$$

   $$= 100 - \frac{100}{n}$$

Formaldehyde reacted/mole melamine = 3.58

∴ Existing formaldehyde in the reactor =

= 5.28 - 3.58 = 170 moles

All the functional groups can be calculated from the analytical results of the resin (butoxi number, degree of polymerisation, reacted formaldehyde) apart from the number of moles of hydrogen and methylol group, because the values depend on the assumption made: methylene ether bridges alone or methylene bridges only.

2. In order to calculate hydrogen and methylol group it was assumed that at the end of the first stage the two types of bridges existed and 28% were methylene ether bridges and 72% were methylene bridges.

This number, 28% was estimated in the following way:

It is known from the data that n = 4.5 for t = 0 and n = 3.6 for t = 8h. That corresponds to a decrease in the number of bridges from 77.8 to 72.2. For t = 8h there are 5.5 moles of bridges less than for t = 0h. But during this 8 hours methylene bridges have been forming. According to the calculated rates from the kinetic data we can estimate that about 12 methylene bridges are expected to be formed in this 8 hours. Therefore at least 17.5 moles of methylene-ether bridges should have existed for t = 0. Considering that by t = 8h, 80% of the methylene-ether bridges have been broken that gives an estimate of 17.5/0.8 22 methylene ether bridges at the beginning of the first stage, corresponding to (22/77.8) x 100 = 28% of bridges.

3. Knowing the proportion of each kind of bridge the number of moles of methylol and hydrogen groups can be calculated.

Methylol group:

From Firth's data:

| t = 0 | Methylol bridge assumption | Methylene-ether bridge assumption |
|---|---|---|
| No of moles of methylol | 130 | 61 |
| no of moles of methylol at end of first stage | 0.28 x 61 + 0.72 x 130 ≃ 110 moles | |

Hydrogen group

| t = 0 | Methylene bridge assumption | Methylene-ether bridge assumption |
|---|---|---|
| no of moles of hydrogen | $z/n = 5 - F + 1/n = 1.61$ | $z/n = 6 - F = 2.39$ |
| | ∴ 1.61 x 100 = 161 moles | ∴ 2.39 x 100 = 239 moles |
| no of moles of hydrogen at the end of the first stage | 239 x 0.28 + 161 x 0.72 ≃ 183 | |

So for the end of the first stage the number of moles of each functional group can be calculated. For M:F:Bu = 1:5.28:5.4 the calculated values were:

| Group | $-CH_2$ | $-CH_2OCH_2-$ | $CH_2OH$ | $-H$ | HCHO | $-CH_2O_4H_9$ | $C_4H_9OH$ |
|---|---|---|---|---|---|---|---|
| No of moles | 55.8 | 22 | 110 | 183 | 170 | 150 | 390 |

Table 4.5 No. of moles of each functional group at the end of the first stage.

3. The volume and water concentration were calculated according to the water removal rate estimated in section 4.3.6.

   Butoxi number = b/n = 1.5

   Reacted formaldehyde = f/n = 3.58

   Polymerisation degree = n = 4.5

   Molecular weight = 1363

   S1 = 25

4. A simulation program for the first stage of reaction alone was run, and the values of K, $K_1$, $K_2$, $K_3$ and $K_5$ were adjusted so that the calculated state of the reaction mixture at the end of the first stage would be met.

5. To ensure that the integration method selected (Runge-Kutta 4th order) was stable several runs with different step height were made. S was selected equal to 6 minutes for which the results are convergent to two decimal figures.

   The suitable values of the kinetic constants for the first stage determined were:

   K (methylolation) = $.105 \times 10^{-2}$ l $\text{min}^{-1}$ $\text{moles}^{-1}$

   $K_1$ (methylene bridge) = $.46 \times 10^{-3}$ l $\text{min}^{-1}$ $\text{moles}^{-1}$

   $K_2$ (butylation) = $.64 \times 10^{-2}$ $\text{min}^{-1}$

   $K_3$ (inverse of butylation) = $.25 \times 10^{-3}$ l $\text{min}^{-1}$ $\text{moles}^{-1}$

   $K_5$ (methylene ether bridge) = $.45 \times 10^{-3}$ l $\text{min}^{-1}$ $\text{moles}^{-1}$

6. For the second state model, several runs were made for the adjustment of the kinetic constant. The data used was Firth's results for the standard charge M:F:Bu = 1:5.28:5.4.

The values of the kinetic constants calculated are:

$K$ (methylolation) = $.13 \times 10^{-2}$ l $min^{-1}$ $moles^{-2}$

$K_1$ (methylene bridges) = $.1 \times 10^{-3}$ l $min^{-1}$ $moles^{-1}$

$K_2$ (butylation) = $.155 \times 10^{-2}$ $min^{-1}$

$K_3$ (inverse of butylation) = $.1 \times 10^{-3}$ l $min^{-1}$ $moles^{-1}$

$K_4$ (break of methylene ether bridges) = $.29 \times 10^{-2}$ $min^{-1}$

## 4.4 Simulation Results

The simulation can be divided in four different categories:

1. Simulation results for different values of the M:F ratio. For this case it was considered that more concentrated solutions of formalin were used in the charge for high M:F ratios. Therefore the volume of the charge was considered in all the cases equal to the standard ratio M:F = 1:5.28, V = 89.2 litres. The results are plotted in fig 4.13 and 4.14.
2. Simulation results for different ratios of M:Butanol. A change in volume of the charge was taken into consideration in this case (fig 4.15 and 4.16).
3. Simulation results for the standard charge M:F:BuOH = 1:5.28:5.4, but with an addition of butanol of 8.1 litres after 2 hours in the second stage of reaction (fig 4.17 and 4.18).
4. Simulation runs with a different proportion of methylene ether bridges. The case of 20% methylene ether bridges was studied.

Figure 4.13 Degree of polymerisation vs reaction time
Simulation results for different value of M:F ratio .

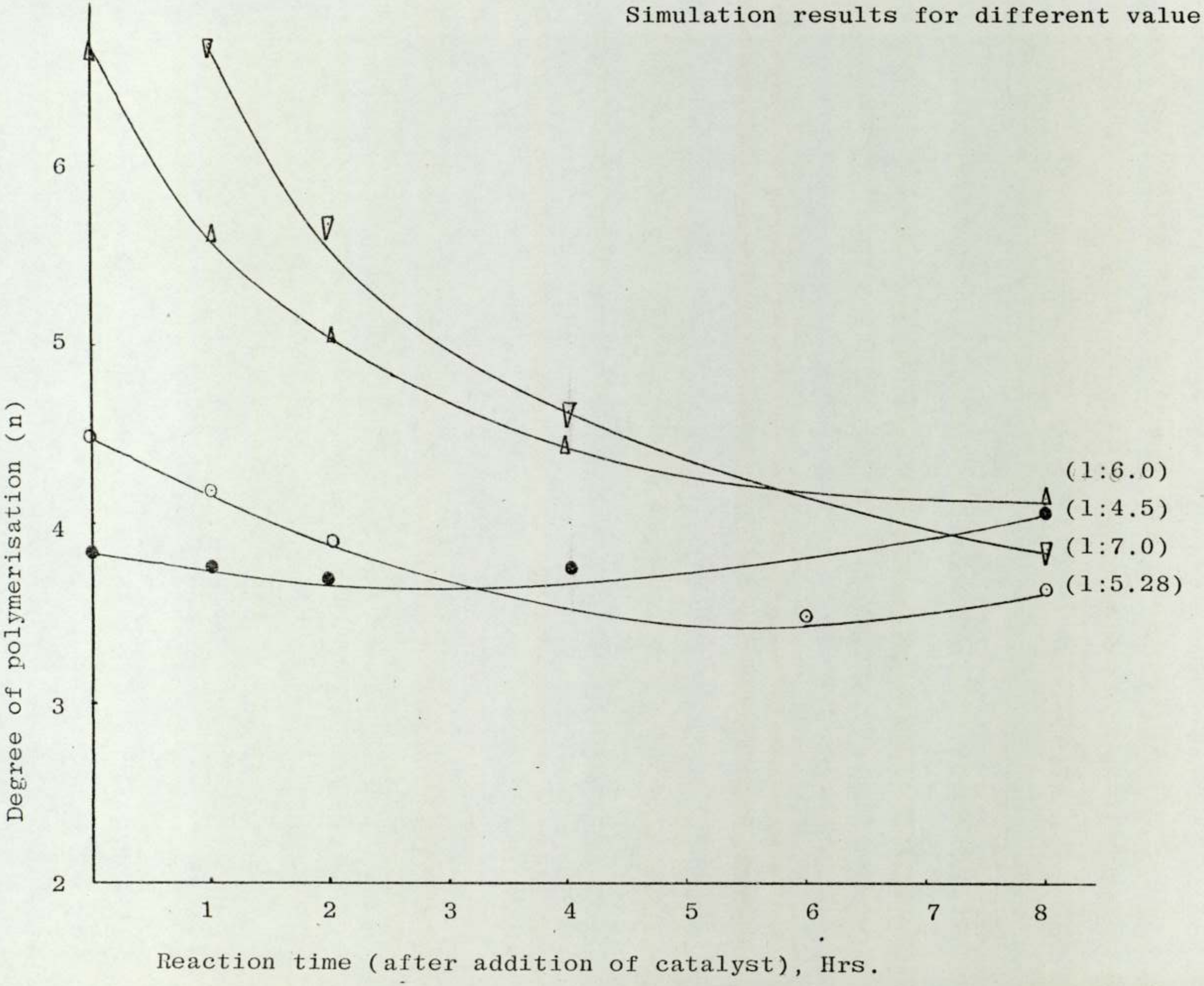


Figure 4.14 Butoxi:melamine vs reaction time
Simulation results for different values of M:F

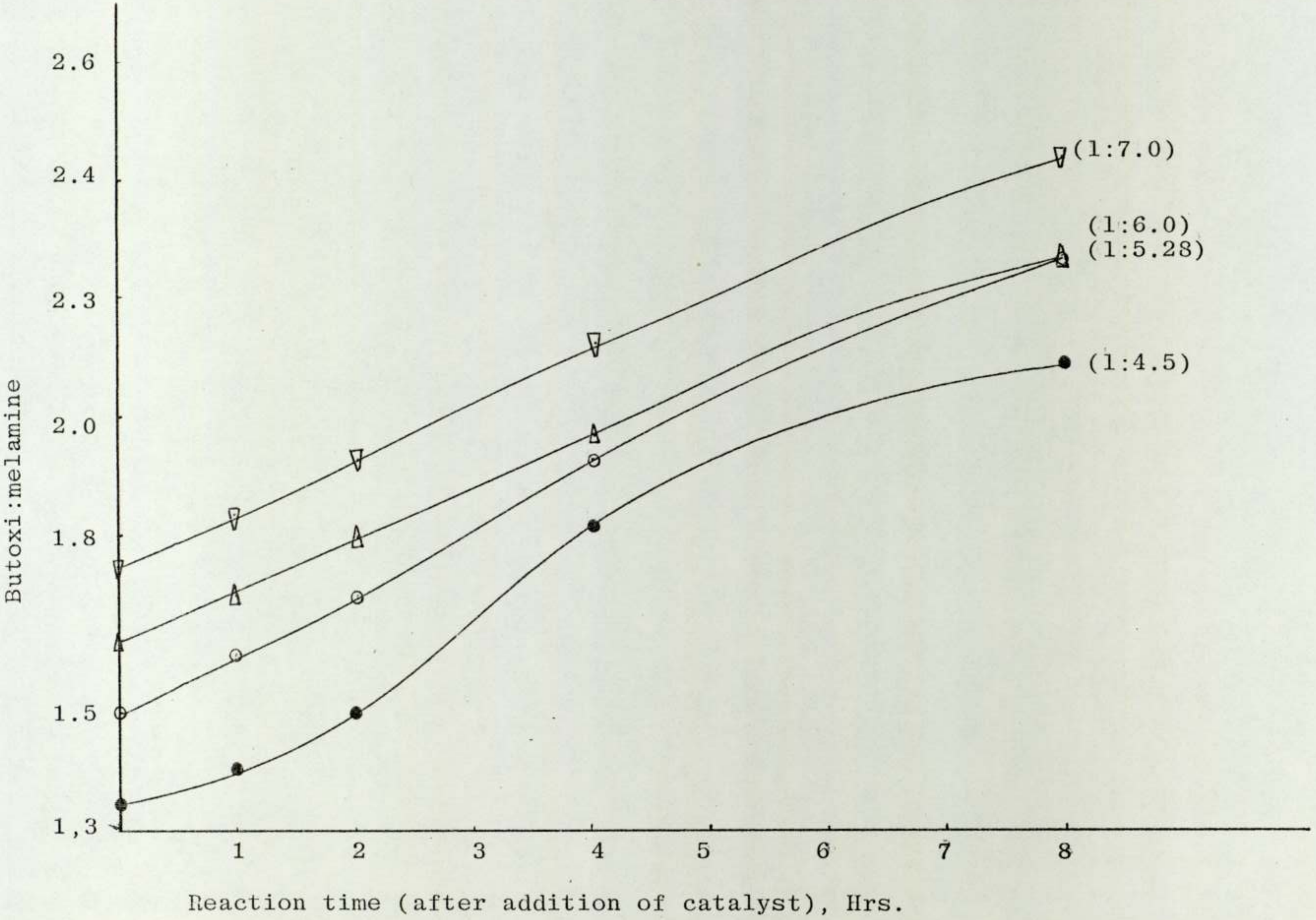


Figure 4.15 Degree of Polymerisation vs reaction time

Simulation results for different values of M:Bu ratios.

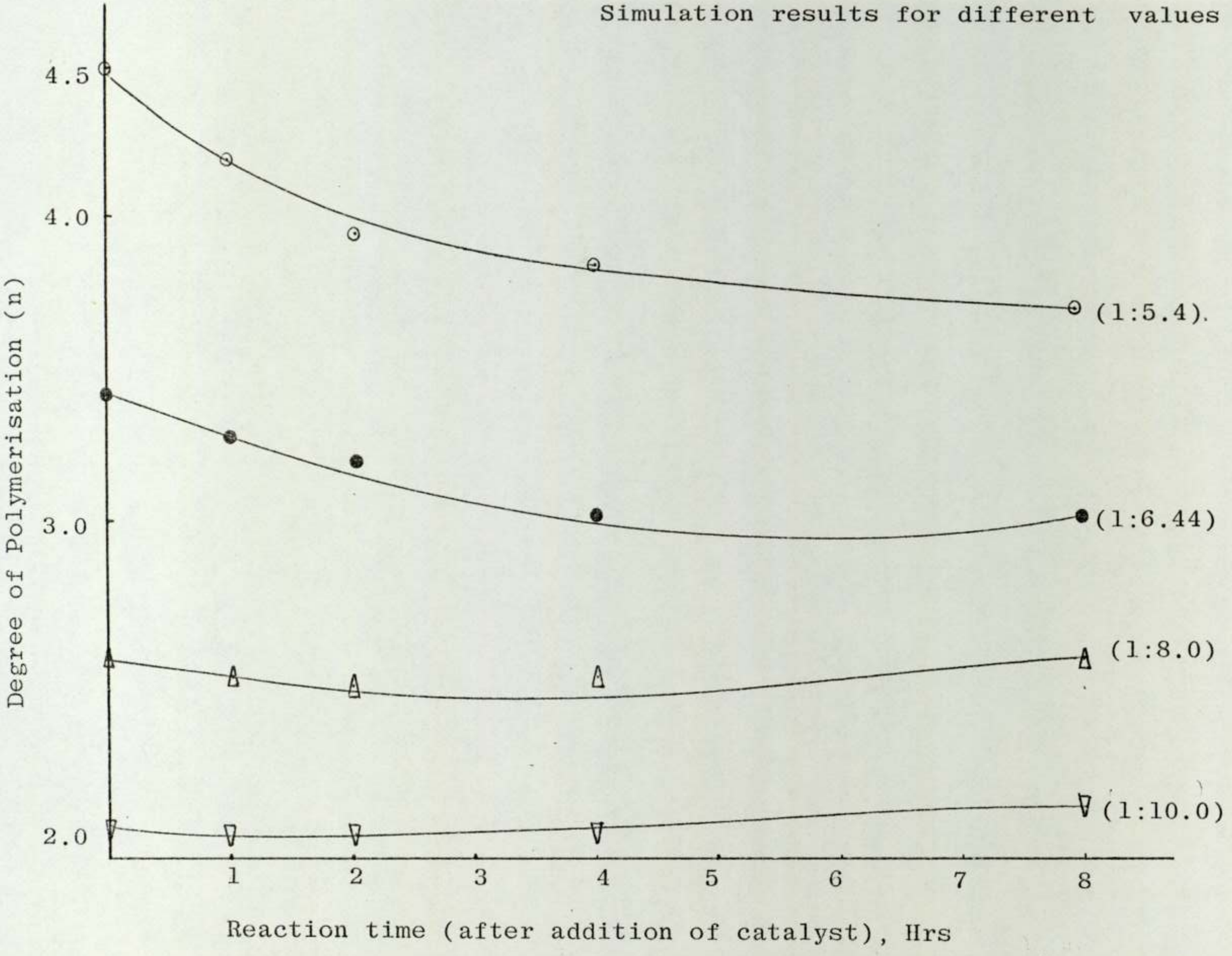


Figure 4.16 Butoxi:melamine vs reaction time
Simulation results for different values of M:B ratios

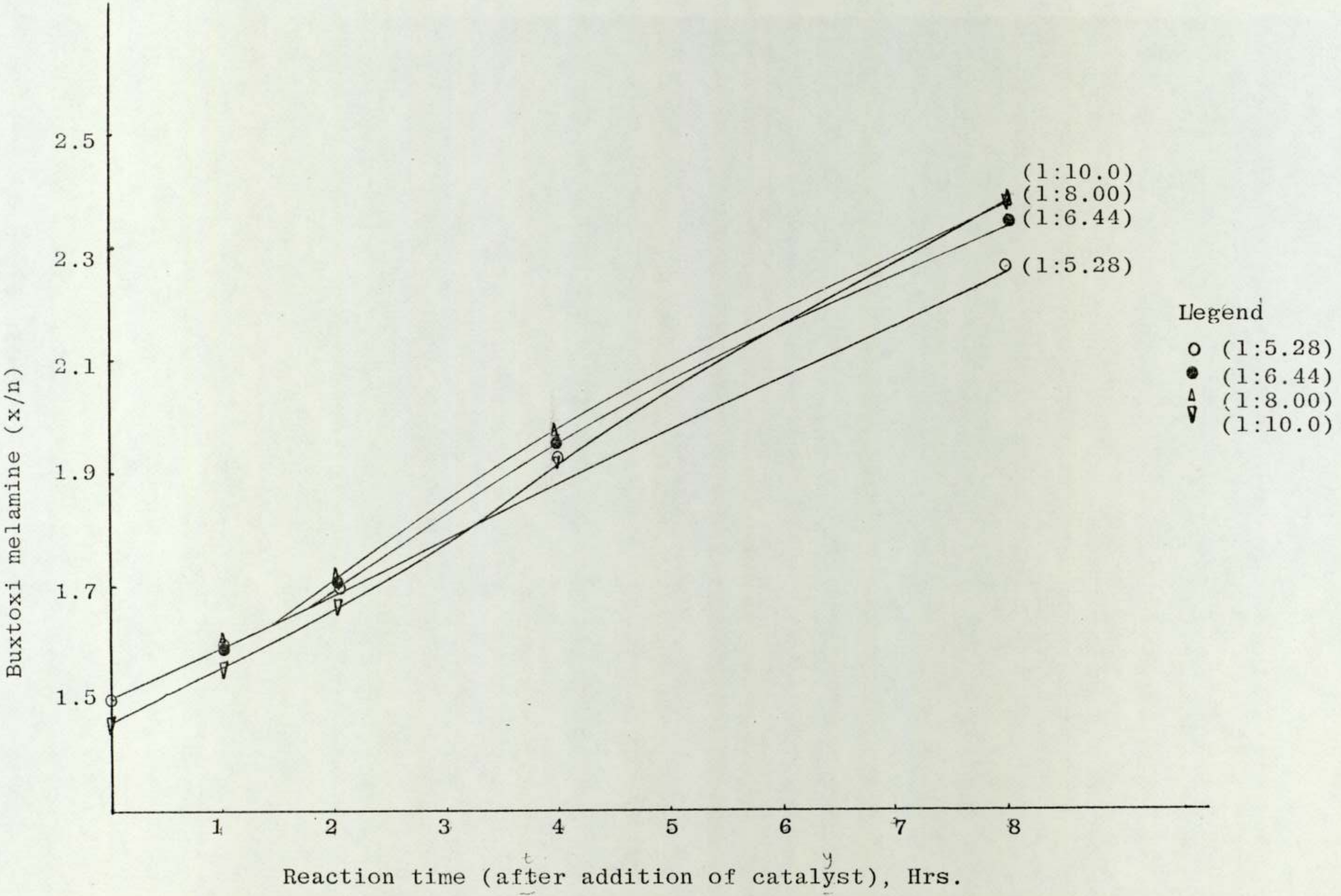


Figure 4.17 Degree of polymerisation vs reaction time
Simulation results.

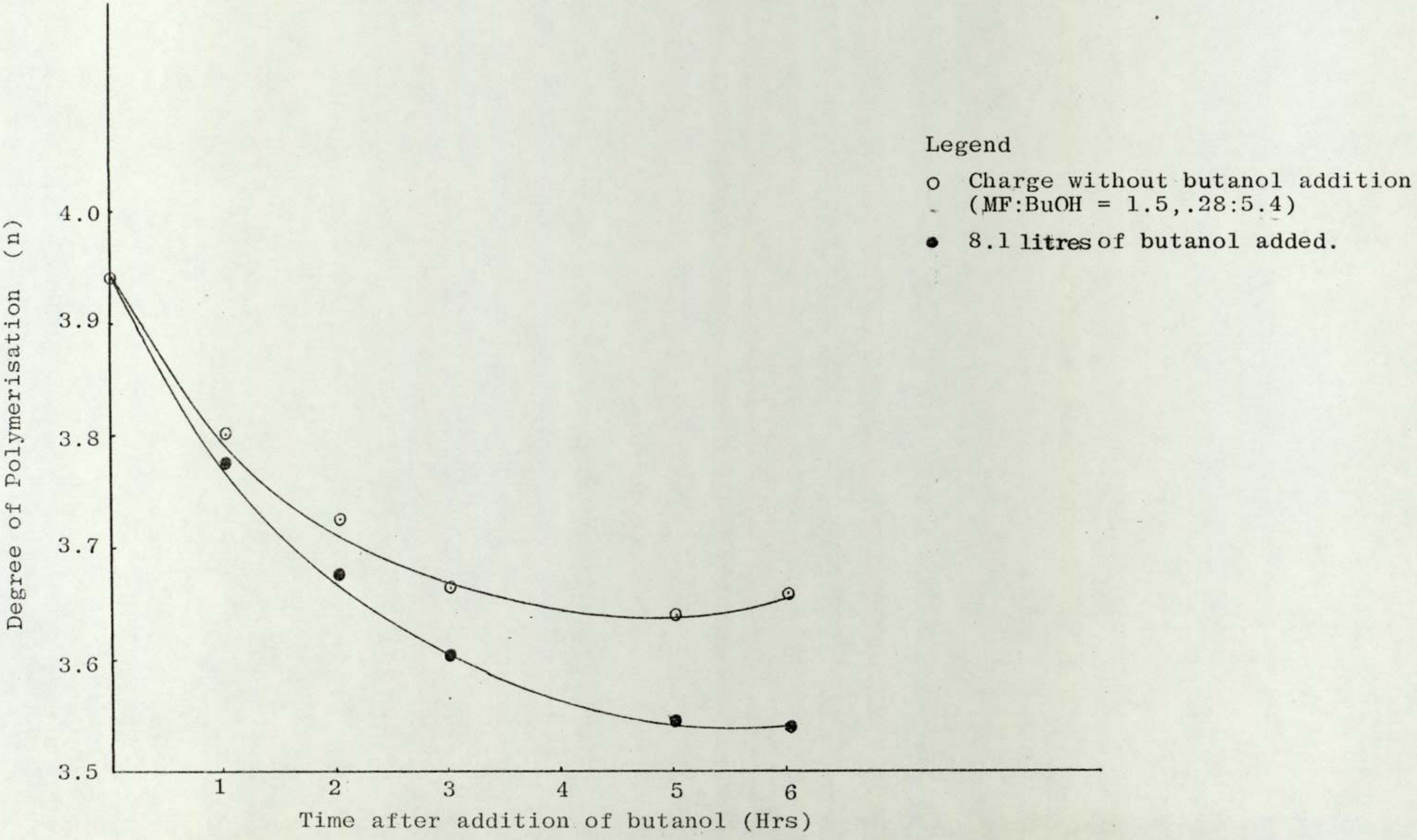
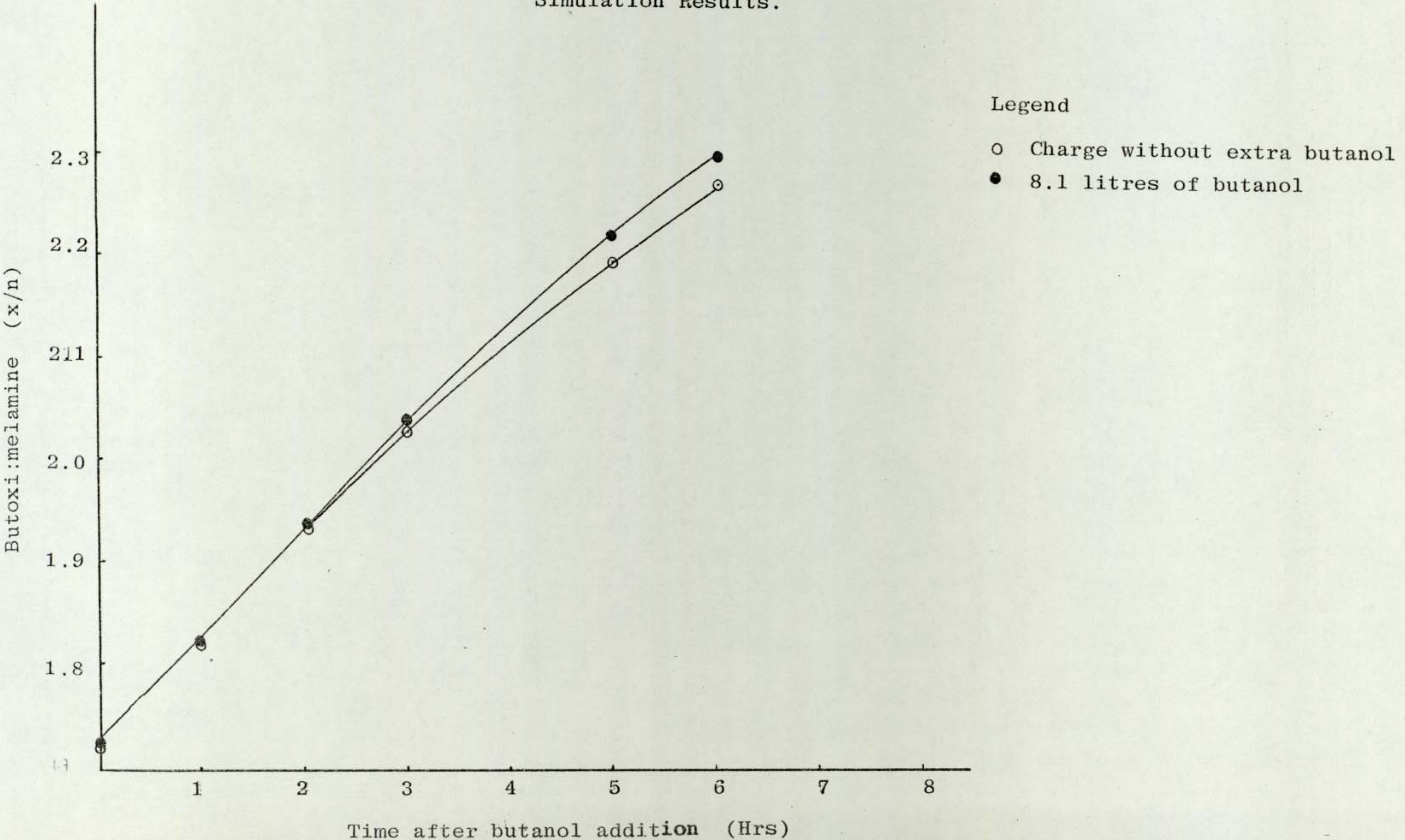


Figure 4.18 Butoxi:melamine vs reaction time
Simulation Results.



## 4.5 Discussion of Results

1. For the first type of simulation results, (M:F charges) fig 4.13 should be compared with fig 4.1 and fig 4.14 with fig 4.4.

   Looking at the degree of polymerisation, there is a very good agreement between the simulated values and experimental values for the standard charge M:F = 1:5.28. For higher ratios it is noticeable that the initial values of the simulated values (up to 4 hours of reactions) are high when compared to the corresponding values of the experimental results. That difference, however, gets small after 4 hours of reaction and for t = 8h the differences are negligible. [This can be explained by the discrepancy of values at the beginning of the second stage due to the lack of information at the first stage of the process. However, after four hours of reaction the values present reasonable agreement]. For the low M:F ratio (1:4.5) the results are very different. In the simulation values it can be noticed a small decrease in the degree of polymerization for the first two hours and a comparatively fast recovery for higher values of time. However, the experimental values show a much faster condensation rate for the low M:F ratio.

   Comparing the butylation rates of the experimental values and simulation values (fig 4.14 and 4.4), there is a very good agreement between the simulated values and experimental values for M:F = 1:5.28 and

M:F = 1:4.5. For M:F = 1:7.0 the simulated values are slightly high especially in the first two hours. The difference, however, tends to decrease and by t = 8h the results are in good agreement. The discrepancy between the results show in this case for M:F = 1:6.00. It is noticeable from the experimental data a high degree of butylation, even larger than for the case M:F = 1:7.0. This result is not logical and should be attributed to some inacuracy in the measurement of the butoxy content. of the resin, Zeiss method for the case M:F = 1:6.00.

In general it can be said that the simulation results are in good agreement with the experimental results with the exception of the degree of polymerisation for low formaldehyde charge. This suggests, that in this case, much higher condensation rates occur.

2. For the second type of simulation results (M:Bu changes) fig 4.7 should be compared with fig 4.15 for the analysis of degree of polymerisation and fig 4.10 should be compared with fig 4.16 for the analysis of the degrees of butylation.

Looking first at the degree of polymerisation, there is a very good agreement between the simulated values and experimental values, especially to the M:Bu = 1:5.4. For the higher ratios the trends of the curves are the same for simulation and experimental values, but is is noticeable that the simulation values present lower values of polymerisation. This effect can be explained if one takes into consideration the fact of the difference between simulation and experimental values getting closer for high reaction times, This proves that the initial difference between the two results is mainly due to inaccurate starting points in the end of the 1st stage.

Comparing the butylation rates of the simulated and experimental results a good agreement is found for the four different ratios. It is interesting to notice in fig4.10 the fact that charges with low M:Bu ratio eventually after extended reaction time leads to higher degrees of butylation. This, however, is not noticeable in the first eight hours of reaction.

In general it can be said that there is a quite good agreement between the experimental and simulation data, and being given good departure points at the end of the first stage the model produces the evolution of the reaction in a realistic way.

3. The third type of simulation runs (fig4.17 and4.18), was tailored to study the behaviour of the model to the common practice in industry of adding butanol at the second stage of the process when the resin is becoming dangerously viscous. It is shown that an increase of 20% of butanol charge has an effect in the polymerisation and butylation reaction balance. In fact, the degree of polymerisation is reduced slightly, and becomes especially noticeable after 3 hours of butanol addition, and the degree of butylation increases, especially after 3 hours of the addition, therefore, an addition of butanol at the

second stage of reaction leads to a less viscous resin and improves white spirit tolerance. The average molecular weight of the resin is reduced if the addition is done.

4. Finally, to study the influence of the proportion or methylene ether bridges at the end of the first stage, simulation runs were done for 20% of methylene ether bridges. In this case the kinetic constants had to be recalculated and the values found were:

1st stage:
$K = .105 \times 10^{-2}$ l $min^{-1}$ $moles^{-1}$
$K_1 = .515 \times 10^{-3}$ l $min^{-1}$ $moles^{-1}$
$K_2 = .64 \times 10^{-2}$ $min^{-1}$
$K_3 = .25 \times 10^{-3}$ l $min^{-2}$ $moles^{-1}$
$K_5 = .31 \times 10^{-3}$ l $min^{-1}$ $moles^{-1}$

2nd stage:
$K = .13 \times 10^{-2}$ l $min^{-1}$ $moles^{-1}$
$K_1 = .65 \times 10^{-4}$ l $min^{-1}$ $moles^{-1}$
$K_2 = .15 \times 10^{-2}$ $min^{-1}$
$K_3 = .1 \times 10^{-3}$ l $min^{-1}$ $moles^{-1}$
$K_4 = .38 \times 10^{-2}$ $min^{-1}$

Compared to the values in section 4.3.7 it is clear that the proportion of bridges has no influence on the methylolation and butylation kinetic constants. As expected the condensation kinetics constants were altered, being $K_1$ reduced (formation of methylene bridges) and $K_4$ increased (reaction of butanol with methylene ether bridges).

The behaviour of the model with these kinetic constants were not substantially altered in respect of M:F and M:Bu.changes.

# CHAPTER FIVE

# THE PILOT PLANT

## 5.1 INTRODUCTION

The manufacture of butylated formaldehyde resins was described in Chapter 3, both in the laboratory and industrial environments. Some minor differences in the operation of the two plants are apparent but the basic concepts of the process are similar. Having obtained the necessary information and experience from these plants it was decided to design, construct and commission an experimental pilot plant at Aston University for the following purposes.

1. To study the effect of a different design of the distillation system on the process,
2. To provide the pilot plant rig with the necessary instrumentation and interface the plant with the Departmental computer so that the automatic control of the process could be studied.

This chapter describes the pilot plant rig including its instrumentation and interface with the computer. The cost of the equipment was supported by B.I.P. Chemicals Limited.

## 5.2 An Overall View of the Pilot Plant

The pilot plant rig can be described schematically by Figure 5.1. As can be seen from the diagram it comprises the plant and its instrumentation at one end and the Departmental Honeywell 316 Computer at the other. In order to establish contact between these two units, some intermediary units are necessary. They are the data conditioning unit and the HADIOS UNIT. The flow of information from the plant to the computer can be described as follows:

Measurements are taken from the plant by different instruments that send analogue signals to the data conditioning unit. In the case of the butylated formaldehyde melamine resin plant, temperature, flow and differential pressure measurements were used. The data conditioning unit converts the analogue signals into voltage signals in the range of 0 to 5 volts, that are sent to the HADIOS UNIT.

HADIOS provides a very flexible method of interfacing the Honeywell 316 Computer to a wide range of input/output devices for on-line application. The analogue output from HADIOS is received by the Computer and through its software responds with a digital signal back to HADIOS. This signal is converted to an analogue signal that after being conditioned acts on the motorized valves of the plant. A more detailed description of the several parts of this plant can be found in the various sections of this Chapter.

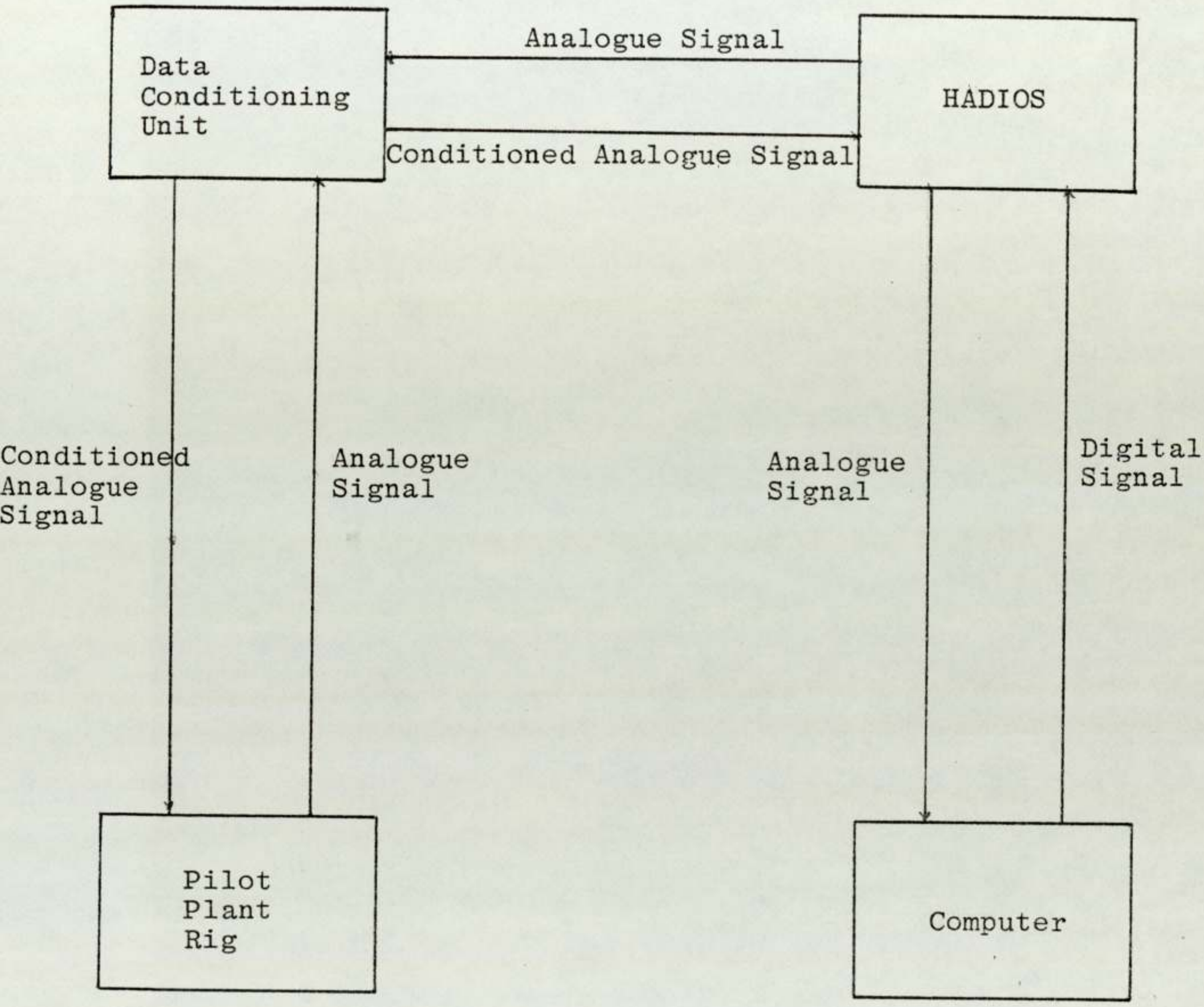


Figure 5.1 Block Diagram of Complete Plant

## 5.3 Distillation System

The basic pieces of equipment of the pilot plant rig comprise a reactor unit and the distillation system involving a reboiler, condenser and separator. The reactor unit was supplied by British Industrial Plastics. It is a batch reactor with a jacket where steam or cooling water can circulate according to the particular requirements of the operation. Due to the corrosive nature of the formaldehyde resins the reactor was constructed in cast iron with the internal parts glass lined. More details of the plant can be found in Appendix 4.

Figure 5.4 is a diagram of the pilot plant rig. It is easily recognised that the layout of the distillation system is different from the plants described in sec. 3.2

In order to improve the water removal process from the reactor a new distillation system was designed for the pilot plant. In this arrangement the wet butanol from the decanter is returned to the top of the distillation column instead of returning it to the reactor. The idea is to minimise the amount of water in the reactor. As the returning alcohol contacts the rising vapours and passes down through the column, separation of at least a portion of the water from the returning wet butanol is obtained. The temperature of the column is controlled by the temperature of the incoming vapours and by heat added by a reboiler attached to the bottom of the column. The temperature in the reboiler is kept high enough (above 110$^{o}$C) so that the bottom stream from the column to the reactor is nearly pure butanol. Butanol's boiling point is 118°C and water boils at 100°C. The two components form an azeotrope with a boiling point of 92.7°C and composition 24.8 mole % of butanol,(Figure 5.2 and Figure 5.3). If the temperature in the reboiler is maintained above 110°C the liquid composition of the mixture will be over 95 mole % of butanol (Figure 5.2), thus substantially "drier" than the top layer of the separator. The distillation column is packed with Raschig rings and is fed with the vapour stream from the reactor by a pipe in its middle section. The temperature of the column raises from bottom to top with the temperature at the top lower than at the bottom. Initially, when a substantial amount of water is present, the azeotrope composition at the top of the column is obtained and the corresponding temperature is 92.7°C.

This distillation system was found to be more efficient than the traditional plants and shorter reaction times were observed. The manufacture of alkylated urea and melamine formaldehyde resins with process alcohol recovery was the subject of a United States patent in 1977. (126 ). The plant that was used comprises a distillation column that works the same way as that used in the pilot plant. It was claimed that when the water content of the returning alcohol ranges from 16 to 20 percent as is typical in present commercial processes the reaction time ranges

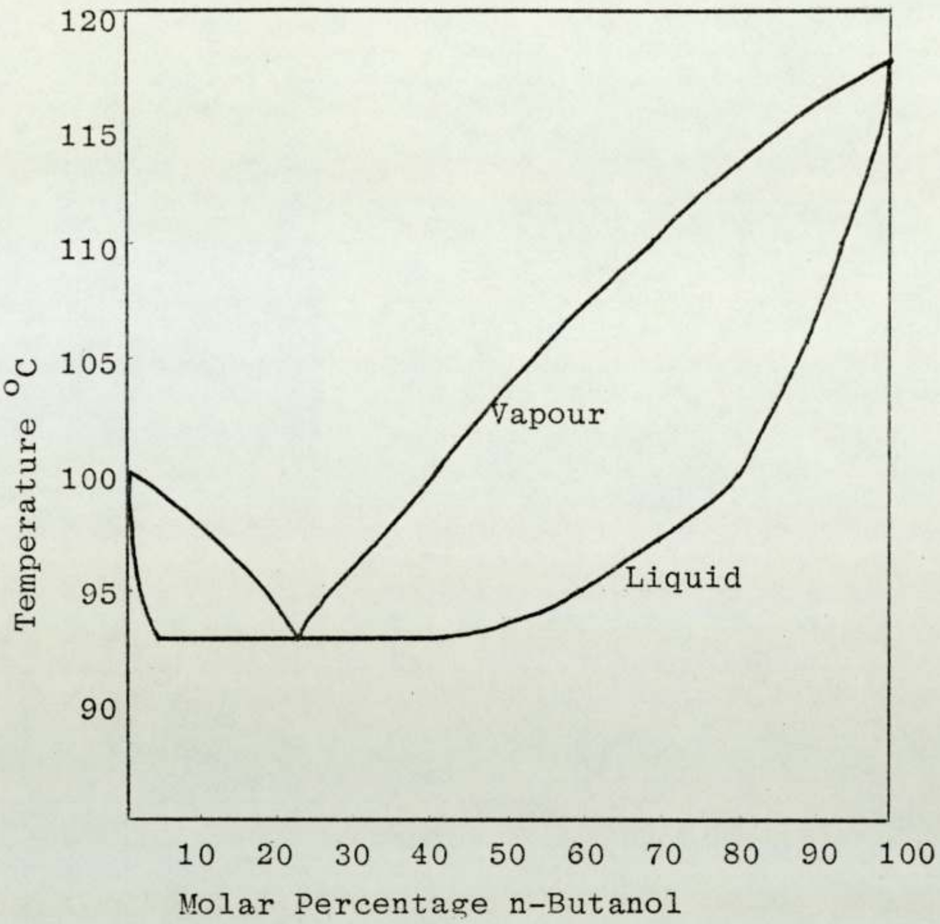


Figure 5.2 Boiling Point - Composition Diagram. n-Butanol - Water (121)

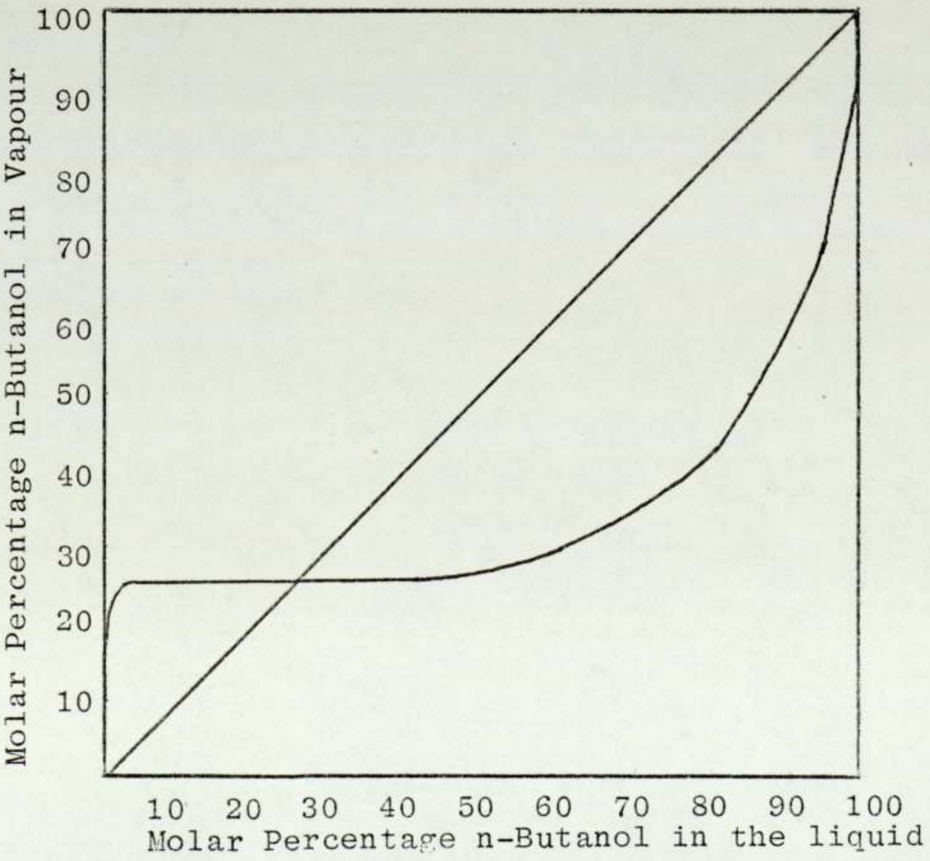
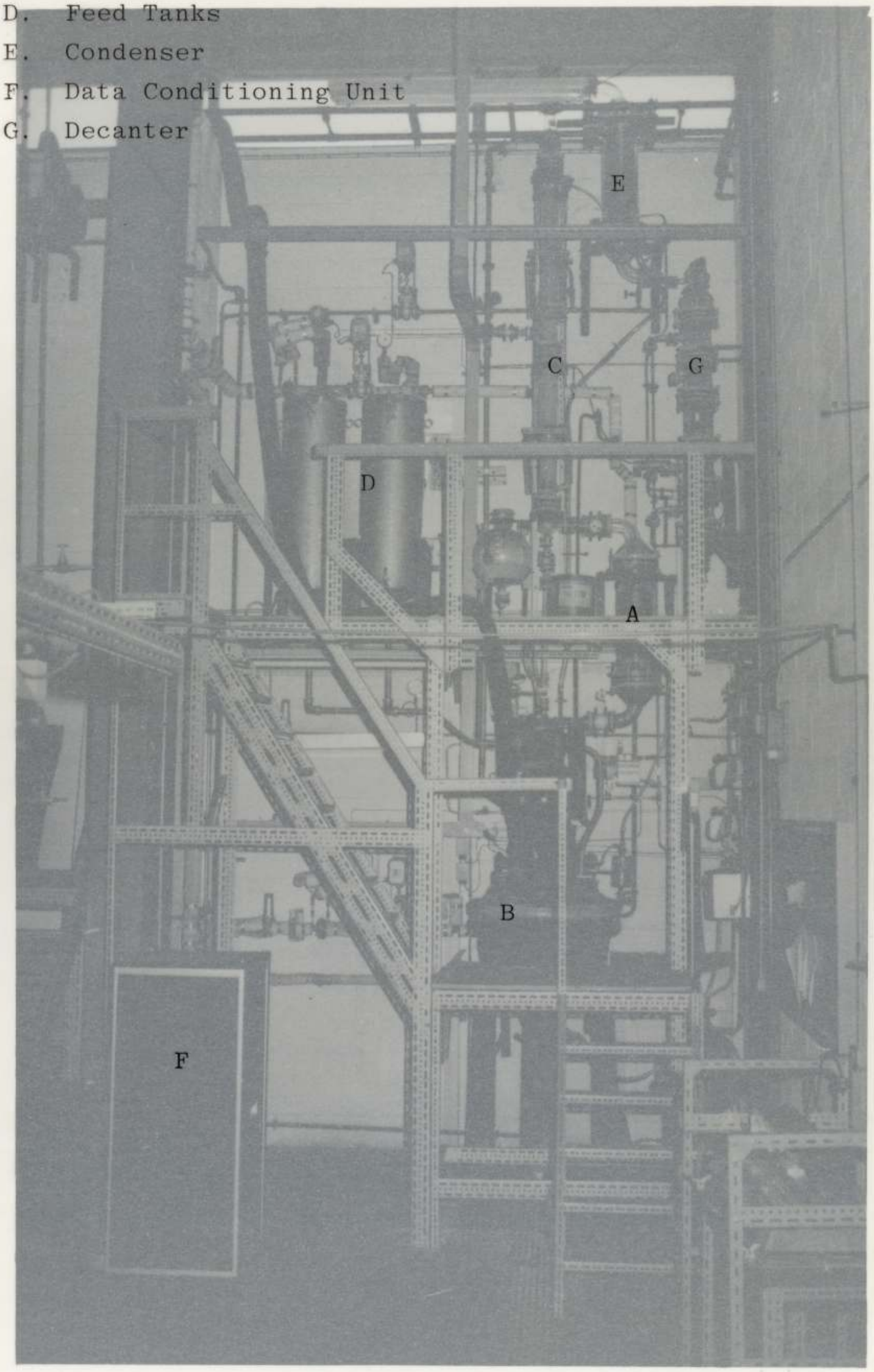
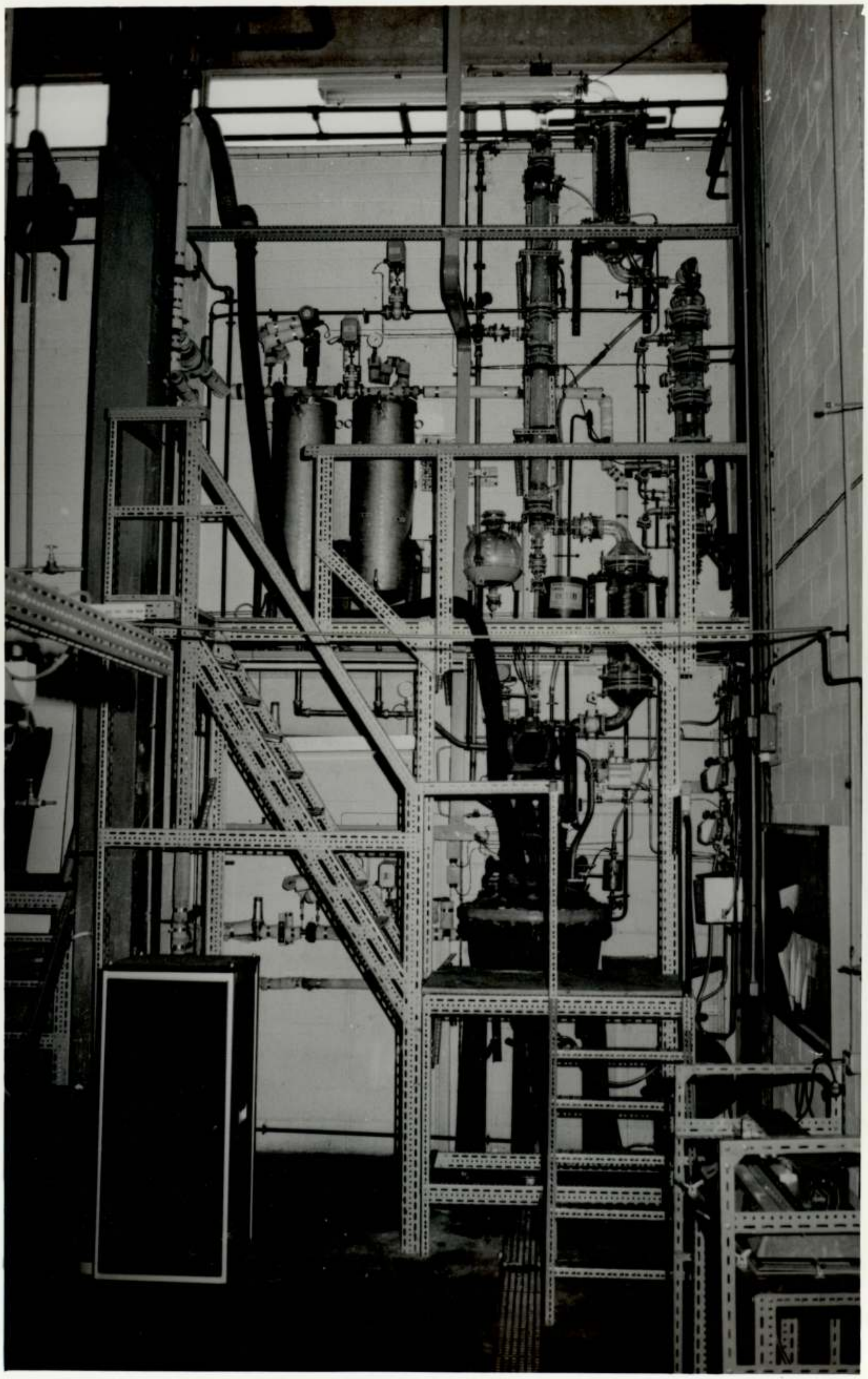


Figure 5.3 Liquid Vapour Equilibrium n-butanol-water

Plate 1

A. Reboiler
B. Reactor
C. Distillation Column
D. Feed Tanks
E. Condenser
F. Data Conditioning Unit
G. Decanter





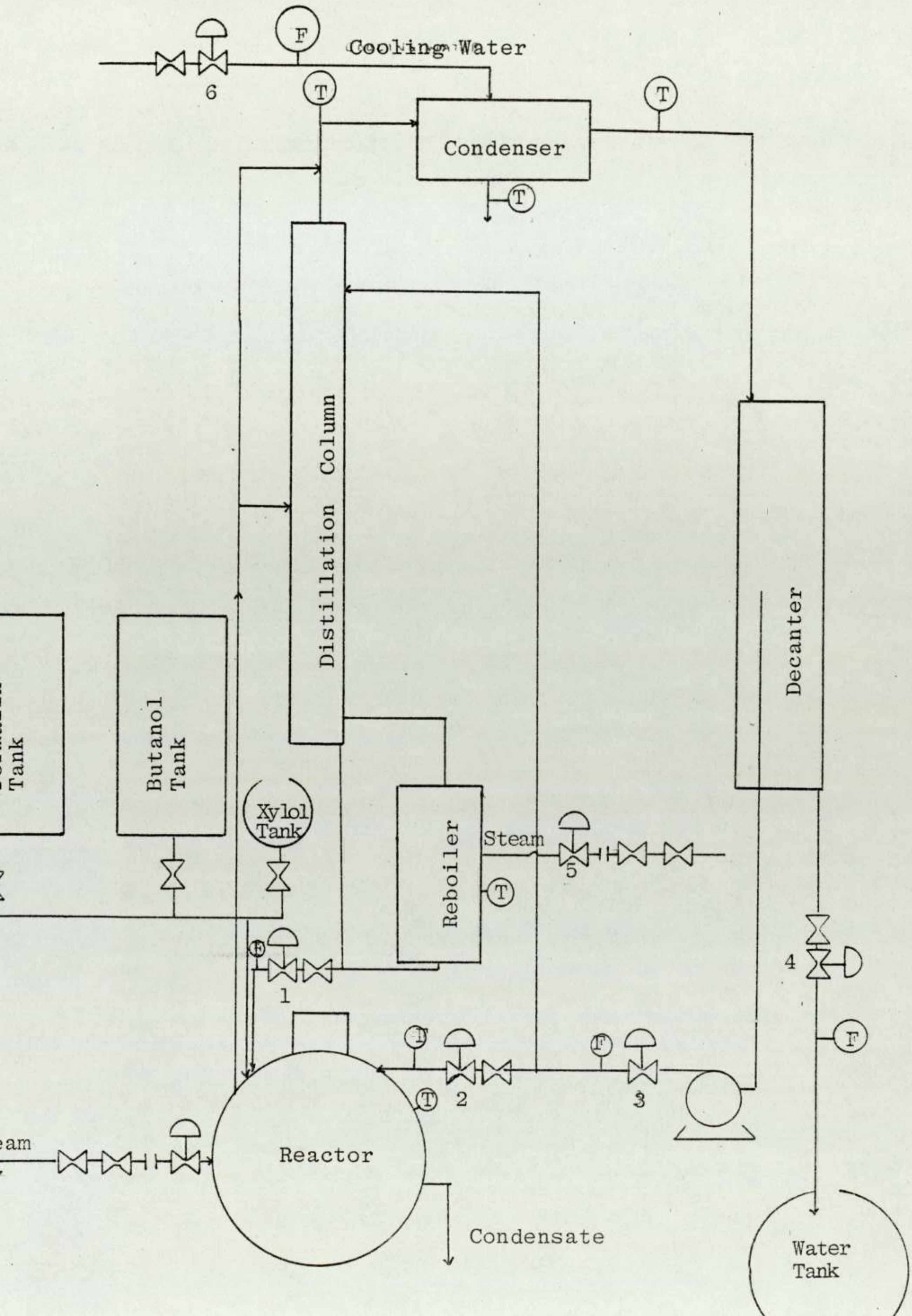


Figure 5.4 Pilot Plant for the Manufacture of Melamine Formaldehyde Resins.

from about 6 to about 18 hours whereas when the water content of the alcohol is reduced to 1% or less, the reaction time is cut in most cases as much as 60%. Although the raw materials used by the authors of the patent differ from the ones used in the pilot plant operation, they used Formol (40% formaldehyde, 50% n-butanol and 7% water) as compared with Formalin (36% formaldehyde, 60% water and 4% methanol) in the pilot plant, it is significant that the right solvent tolerance was obtained in the pilot plant runs after four hours of the second stage of reaction i.e., after the acid catalyst addition. This shows that the condensation and butylation reactions proceed faster in the the pilot plant when compared to industrial plants, due to a reduced water content in the reactor in the former case.

The details of the physical characteristics of the main units of equipment are presented in Appendix 4.

## 5.4 Process Instrumentation

The process instrumentation comprises the following measurements:

(i) Differential Pressure measurements for level control
(ii) Flow Measurements
(iii) Temperature Measurements

Due to the low flow rates in the pilot plant turbine flow meter were used for the flow measurements. The temperature measurements were constructed by the Department electricians. By this means it was possible to keep the cost of instrumentation at acceptable low levels, so that computer control became a more competitive alternative.

### 5.4.1 Differential Pressure Cells

One of the factors influencing the selection of pressure transmitter devices was flexibility, i.e. the instrumentation chosen for the pilot plant should, whenever possible be appropriate for use in the industrial environment, especially in B.I.P. plants. Since most of the instrumentation used at B.I.P. Plants was supplied by Foxboro, the pressure cells were selected from the range of this company's products. Five pressure cells were acquired for the following streams of the pilot plant (See Figure 5.4):

(i) Two pressure cells for the separator where two level controllers were implemented (Fig. 5.4). The need for controlling two levels is justified as follows; (a) the total amount of liquid in the separator needs to be controlled to avoid overflow and spillage of the top layer of the separator. (b) The interface of the two phases in the separator must be controlled because if the amount of liquid phase increases over the level where the suction pipe for the reflux to column is, the return to the column will be an undesirable aqueous phase instead of the butanolic phase as intended.

(ii) One pressure cell for a level control of the reboiler. The reboiler should never be allowed to run dry of liquid (Figure 5.4)

(iii) Two pressure cells to be used in conjunction with orifice plates in the steam lines to the reactor and reboiler so that the steam flow rate can be determined (Figure 5.4)

The differential cell transmitter is an electronic instrument that continuously measures differential pressure and transmits this pressure as a proportional milliampere signal. The output signal from the transmitter is a 4 to 20 mA dc signal, that is directed to the data conditioning unit where it is converted to a 0 to 5 volt signal to be read by HADIOS. The calibration of the five transmitters was done by the manufacturer and the accuracy is ± 0.2% of calibrated span. The calibrated spans are given in Table 5 with a signal of 4 mA corresponding to the lower limit of the calibrated span and 20 mA corresponding to the top limit of the span.

| Location of the Pressure Cell Transmitter. | CALIBRATED SPAN | |
|---|---|---|
| | (In of $H_2O$) | m b |
| Decanter | 20 - 60 | 48 - 144 |
| Decanter | 17 - 42 | 40.8 - 100.8 |
| Reboiler | 0 - 25 | 0 - 60 |
| Steam Line to Reactor | 0 - 25 | 0 - 60 |
| Steam Line to Reboiler | 0 - 25 | 0 - 60 |

Table 5.1 Calibrated Spans of Differential Pressure Cell Transmitters.

### 5.4.2 Turbine Flow Meters

Lowflo transmitter is a precision instrument for the measurement of extremely low rates of liquid as found in the pilot plant. The standard five measuring range is 3 litres to 60 litres/hr and the body material is A.I.S.I. 316 stainless steel. The design of the transmitter is simple and consists of a rotor cartridge and a detector cap. The speed of rotation is proportional to the liquid velocity. Small ferrite pellets are incorporated in the tips of rotor valves and the inductance of a pick-off coil which is located in the detector cap varies with the proximity of the ferrite tipped valves. The small variation in inductance is sensed by a phase lock loop detector and the resultant low frequency signal drives a reed relay in the converter, that is placed in the data conditioning cabinet adjacent to the plant. The output from the converter is 0 - 20 mA. The appropriate selection of resistances and capacitors in the data conditioning units converts this signal to o - 5 volts, thus the correct output for HADIOS. In figure 5.5 a scheme of a turbine flowmeter is presented. The accuracy of the transmitter is better than 1% of the full scale, i.e. 0.6 l/h, more than enough for the requirements of the pilot plant.

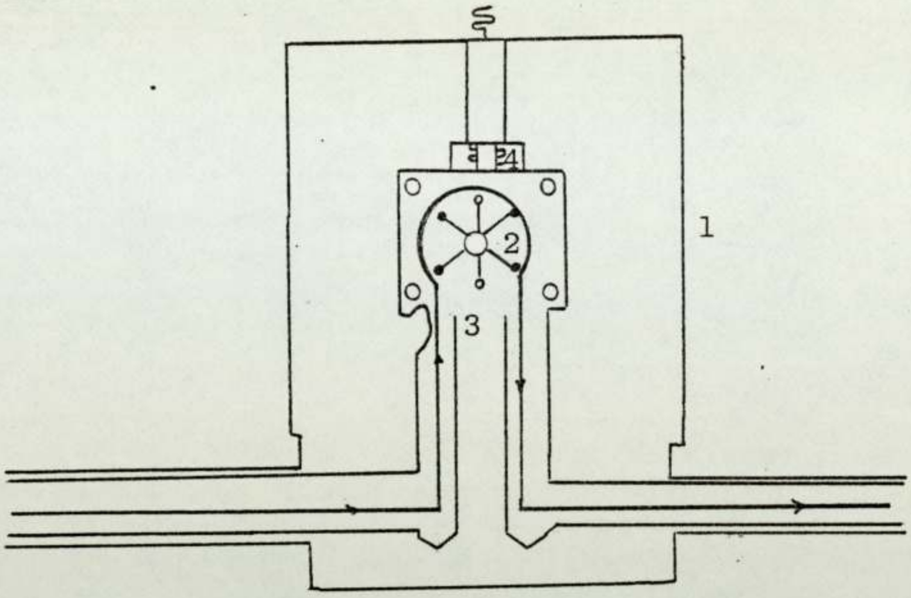


Figure 5.5 Turbine Flowmeter

(1) Body

(2) Rotor

(3) Ferrite Pellet

(4) Pick Off Coil.

Four flow measurements have been used in the pilot plant, in the following locations:

(i) Water off-take line. The knowledge of the flow at a given time of the process is an important piece of information since it gives an indication of the progress of the batch. At the first stage of the process the water removal rate is much higher because of the large amount of water loaded in the reactor as formalin. When the total amount of water introduced in the form of formalin solution has been removed the acid catalyst is added and the so called second stage of reaction is initiated. At this stage the only water removed corresponds to the water formed by the condensation and butylation reactions which is present in small amounts.

(ii) Bottom of the column. It measures the flow of dry butanol to the reactor and shows how the level in the reboiler is changing with time.

(iii) Reflux to reactor and distillation column. The flow meters are located after the centrifugal pump that returns wet butanol (top phase) to either the reactor or the column. If all the top layer of the decanter is directed to the reactor the operation of the pilot plant reproduces the conditions in industrial plants whereas if the stream is returned to the distillation column the operation is the one described in Sec 5.3.

### 5.4.3 Temperature Measurements

Five temperature measurements were used in the following locations:

(i) Condenser. Temperature measurement of the liquid stream going to the decanter.

(ii) Top of distillation column. Temperature measurement of the vapours leaving the column.

(iii) Cooling water at condenser

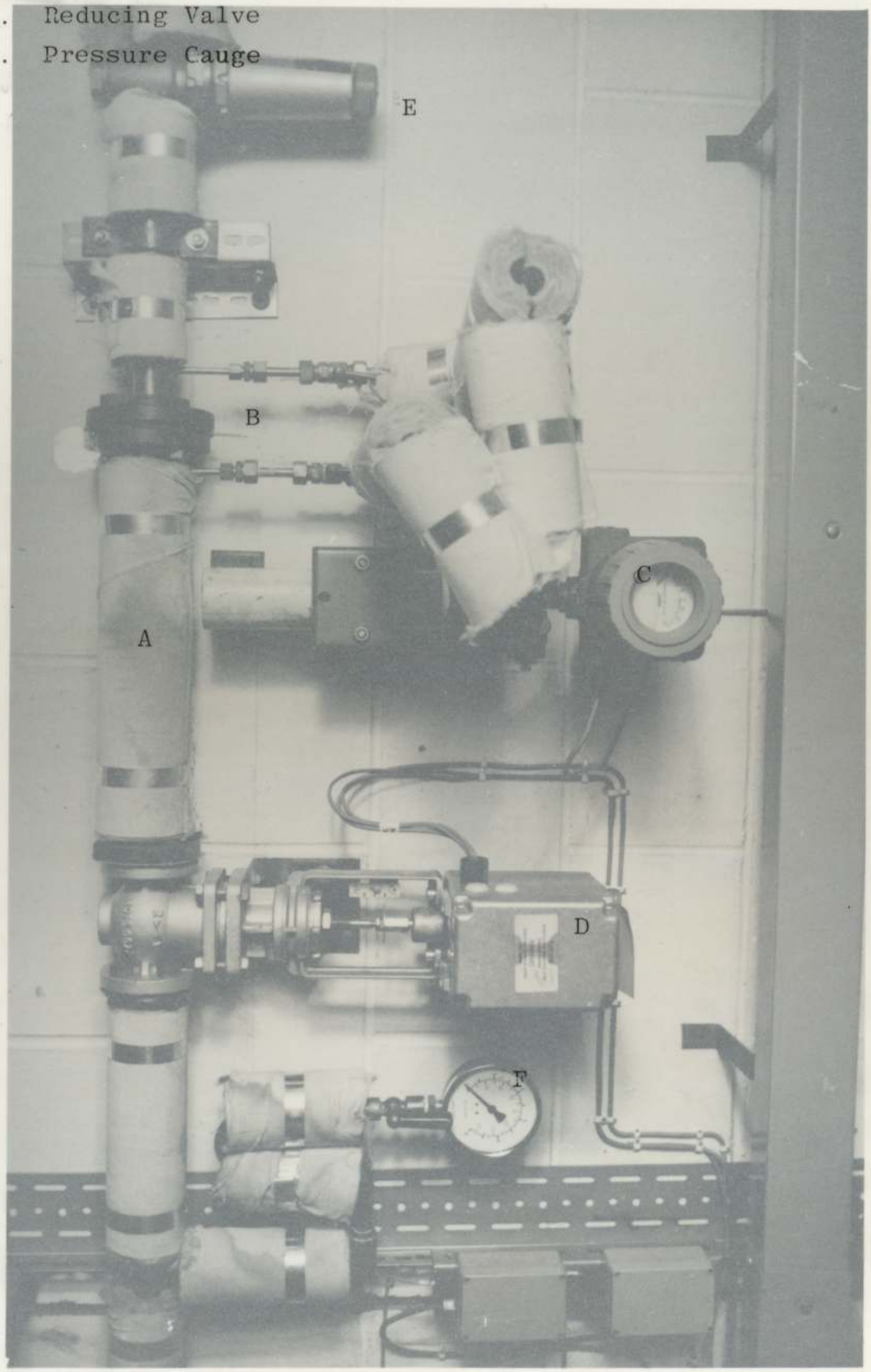
(iv) Reactor. Temperature measurement of the reaction mixture.

(v) Reboiler temperature measurement of the liquid in the reboiler.

The thermocouples used were designed by two of the electronic technicians of the Department at Aston University and they combine good accuracy and almost noise-free readings with economical construction. The thermocouples are a nickle-chromium aluminium alloy with the internal power supply provided by long-life batteries. The reference temperature is provided by the melting point of ice in a heat proof container, that is refilled with fresh ice in contact with water when necessary. During the length of a full run of the plant, there was no need to refill the container with additional ice. High performance operational amplifiers were used to limit the electrical signal to the range of 0 to $\pm 5$ volts corresponding to a digital output from the ADC in the range of 0 to $1023_{10}$ (10 bit resolution). The amplifiers gain of 1000 was obtained by an adequate selection of resistors. These thermocouples have shown excellent reproducibility in calibration with an accuracy of $\pm$ $0.2^{o}C$. The calibration of the thermocouples is shown in Appendix 5.

Plate 2

A. Steam Line
B. Orifice Plate
C. Pressure Cell
D. Electrical Motorised Valve
E. Reducing Valve
F. Pressure Gauge



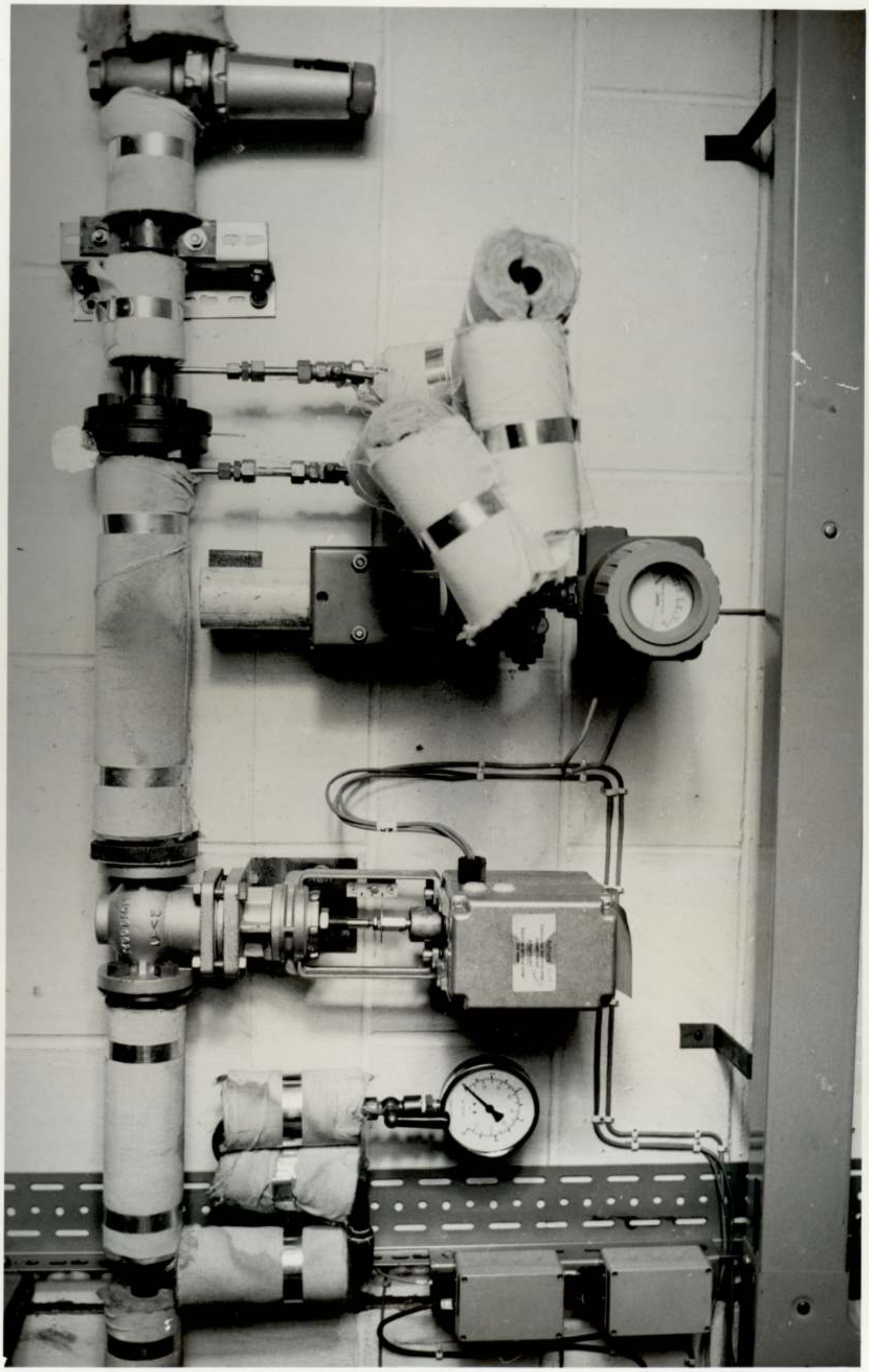
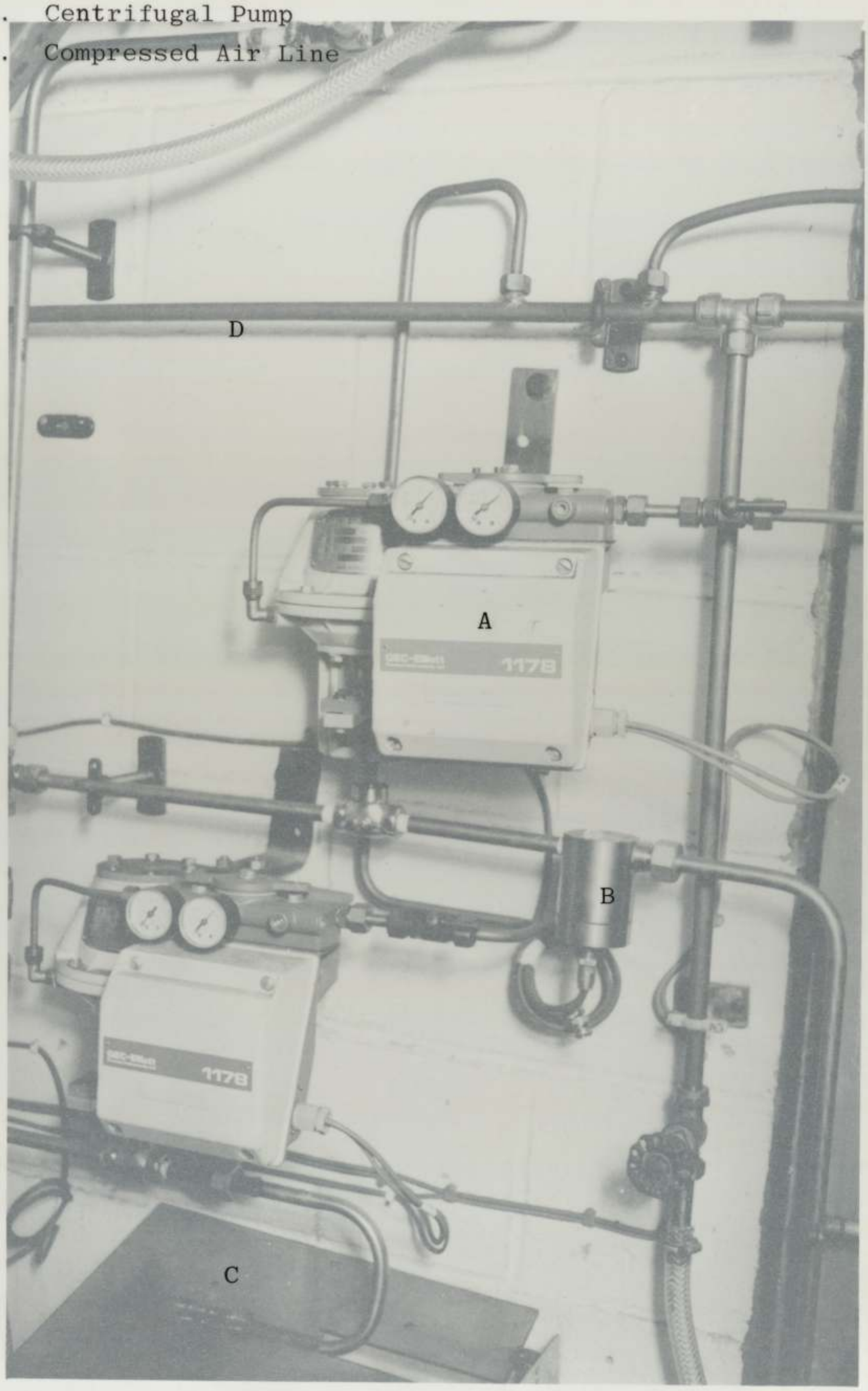
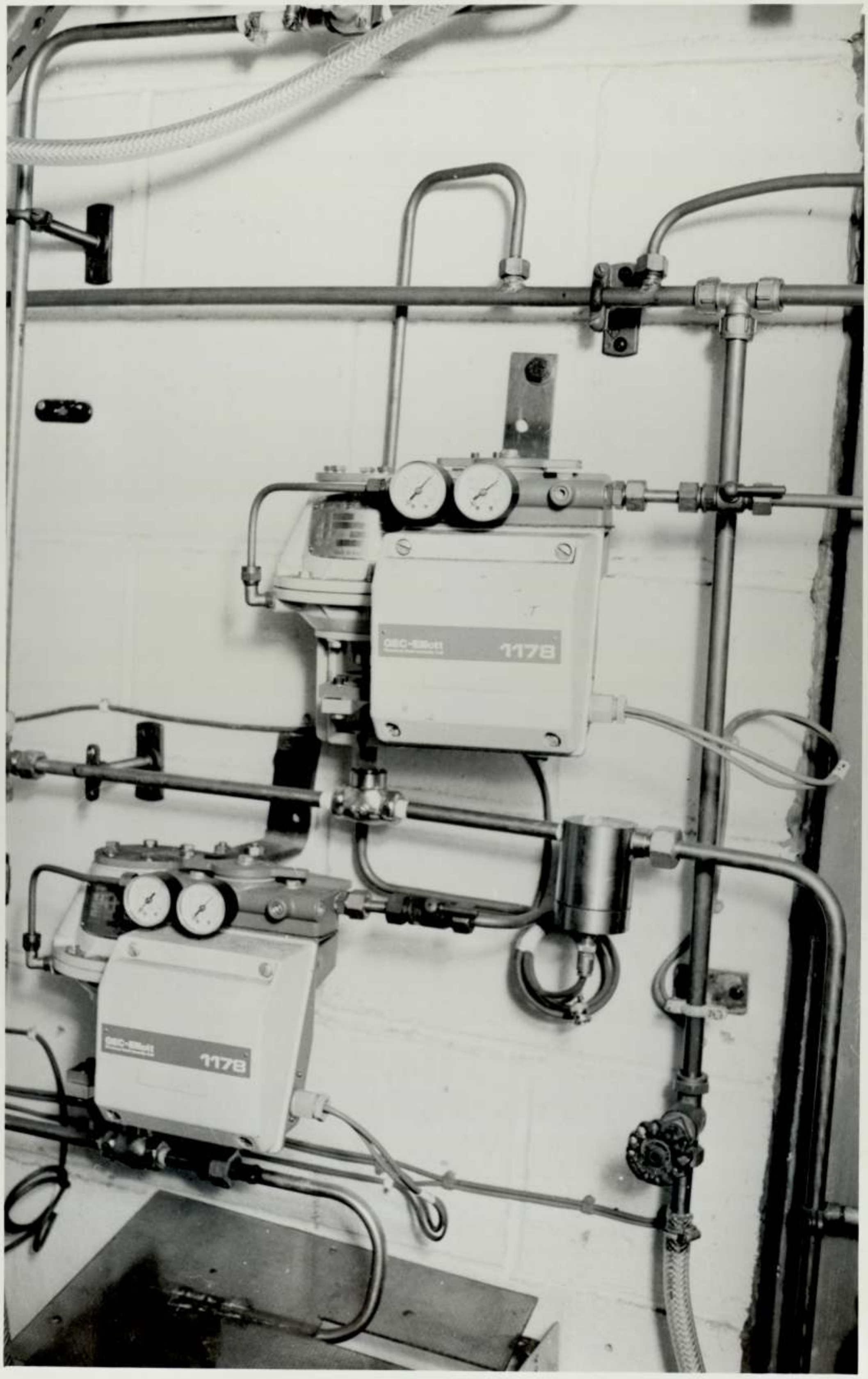


Plate 3

A. Pneumatic Valve
B. Turbine Flowmeter
C. Centrifugal Pump
D. Compressed Air Line

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## 5.5 Plant Computer Interface

For the interface of the pilot plant and the Honeywell 316 Computer the Honeywell Analogue/Digital Input-Output System (HADIOS) was used. HADIOS provides an economic and flexible method of interfacing this type of computer to a range of input-output devices in on-line applications. It consists of a controller, connected to the computer input-output data and control lines which generates subsidiary data, addresses and controls for up to 15 different subinterfaces. The operation of the subinterfaces is initiated by the output of control signals from the computer to the HADIOS controller. The output signals are implemented by means of programmable commands. The details of the instructions for the operation of HADIOS can be found in the HADIOS manuals and in Webbs work (125) A wide range of standard sub-interfaces is available. These, together with the modularity of construction, allow HADIOS to be configurated simply to meet the particular requirements of each application.

In the Department, a single channel of the analogue to digital converter (ADC) is used to process 48 analogue input channels from 3 multiplexers. The ADC works sequentially converting one input at a time. The circuit is reset each time an input is converted. The inputs to the ADC are conditioned analogue inputs in the range of 0 to 5 volts and the outputs from ADC to HADIOS are binary integers with a 10 bit resolution, i.e. 0 to 1023.

The information from the computer to the control valves is transmitted via a line selector and a Digital to Analogue Converter with 8 bits resolution corresponding to 0 to 10 volts. Figure 5.6 shows schematically the interface of the plant to the Honeywell 316 Computer. At the moment the following subinterfaces are available in the Department:

(1) 48 Analogue inputs
(2) 3 Counters
(3) 2 Digital Inputs
(4) 2 Digital Outputs

For the interfacing of the resin plant with the computer only a digital output and analogue inputs have been used. The allocation of the analogue and digital channel to each piece of instrumentation is given in Tables 5.2, 5.3 and 5.4.

| DIGITAL OUTPUT CHANNEL NUMBER | LOCATION |
|---|---|
| A1 | BOTTOMS, motorised valve. |
| A2 | RETURN REACTOR; motorised valve |
| A3 | REFLUX TO COLUM; motorised valve |
| A4 | WATER OFF-TAKE LINE; motorised valve |
| A5 | STEAM TO REBOILER; motorised valve |
| A6 | COOLING WATER; motorised valve |
| A7 | STEAM TO REACTOR; motorised valve. |

Table 5.2 Digital Output Channels

| ANALOGUE CHANNEL NUMBER | LOCATION AND DESCRIPTION |
|---|---|
| 1 | WATER OFF TAKE STREAM<br>TURBINE FLOW METER |
| 2 | REFLUX TO COLUMN<br>TURBINE FLOW METER |
| 3 | REFLUX TO REACTOR<br>TURBINE FLOW METER |
| 4 | BOTTOMS<br>TURBINE ~~TO~~ FLOW METER |
| 5 | COOLING WATER LINE<br>TURBINE FLOW METER |
| 6 | DECANTER-AQUEOUS PHASE<br>PRESSURE CELL |
| 7 | DECANTER-TOP PHASE<br>PRESSURE CELL |
| 8 | STEAM LINE TO REBOILER<br>PRESSURE CELL |

Table 5.3 Analogue Input Channels.

| ANALOGUE CHANNEL NUMBER | LOCATION AND DESCRIPTION |
|---|---|
| 1 | WATER OFF TAKE STREAM<br>TURBINE FLOW METER |
| 2 | REFLUX TO COLUMN<br>TURBINE FLOW METER |
| 3 | REFLUX TO REACTOR<br>TURBINE FLOW METER |
| 4 | BOTTOMS<br>TURBINE FLOW METER |
| 5 | COOLING WATER LINE<br>TURBINE FLOW METER |
| 6 | DECANTER-AQUEOUS PHASE<br>PRESSURE CELL |
| 7 | DECANTER-TOP PHASE<br>PRESSURE CELL |
| 8 | STEAM LINE TO REBOILER<br>PRESSURE CELL |

Table 5.4 Analogue Input Channels
(Continuation)

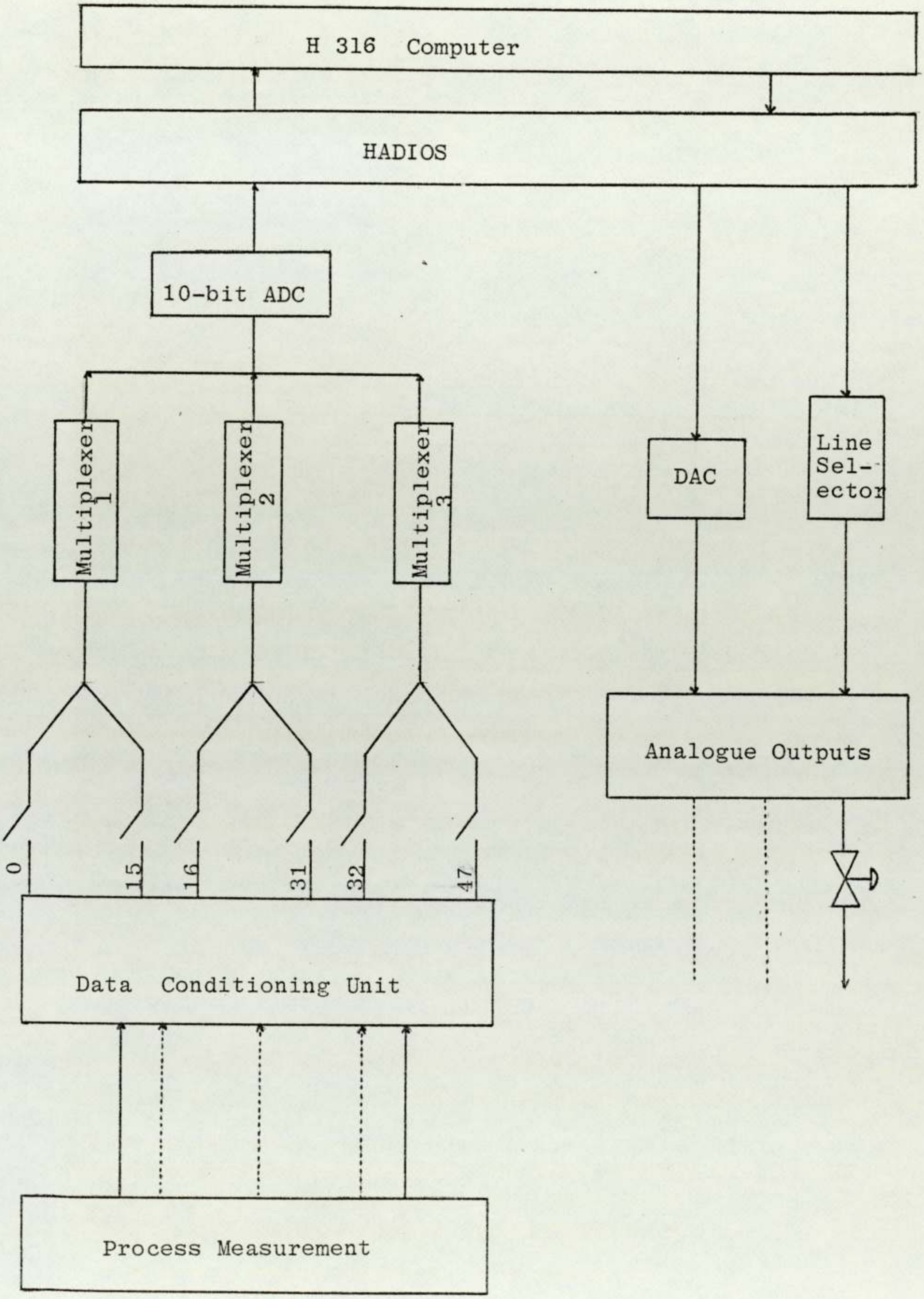


Figure 5.6 Diagram of Computer Plant Interface.

## 5.6 Data Conditioning Unit

The data conditioning unit is located in a cabinet by the pilot plant rig for convenience to the plant operator. This unit was built by the Departmental electricians. Its function is to convert the signals from the various measurement devices to a compatible form for HADIOS and also the signals from the computer to the motorised valves.

This unit comprises:

(i) Power supply for the transducers and motorised valves

(ii) Line drivers for the transmission of digital signals

(iii) The manual/automatic switches for the valves with indicator lights.

(iv) The converters for the turbine flow meters. The impulses received from the flow transmitters are converted into a signal 4 to 20 mA that is conditioned by a series of resistors and amplifiers into a voltage signal in the range of 0 to 5 volts. D.C.

(v) Flow rate indicator with a moving coil meter scaled in l.p.h. covering the full range, i.e. 0 - 60 l/h, of the transmitter.

(vi) Battery charger for thermocouples

(vii) Four sense switches

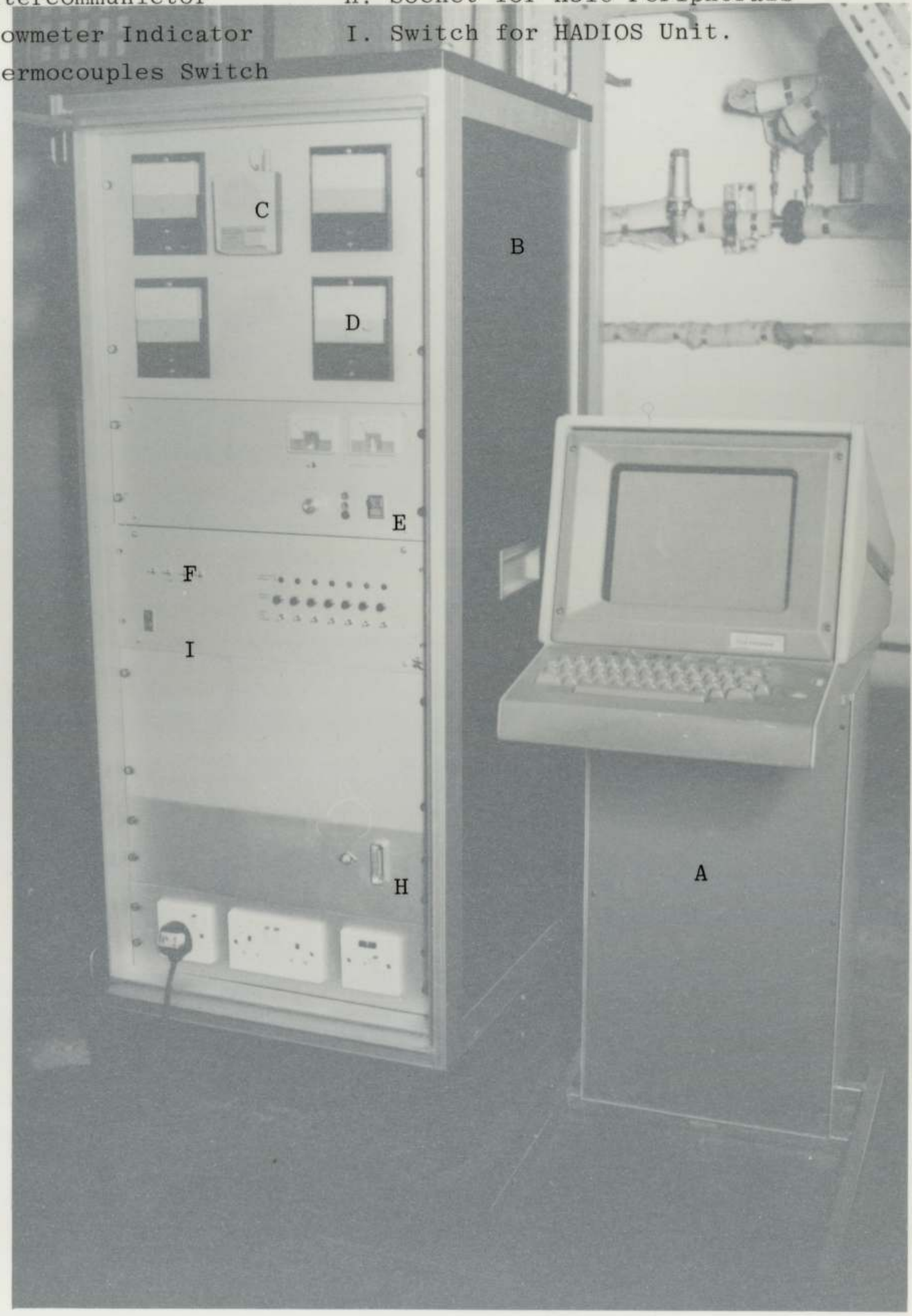
(viii) Three dual input cards for conditions of the analogue signals from the pressure cells.

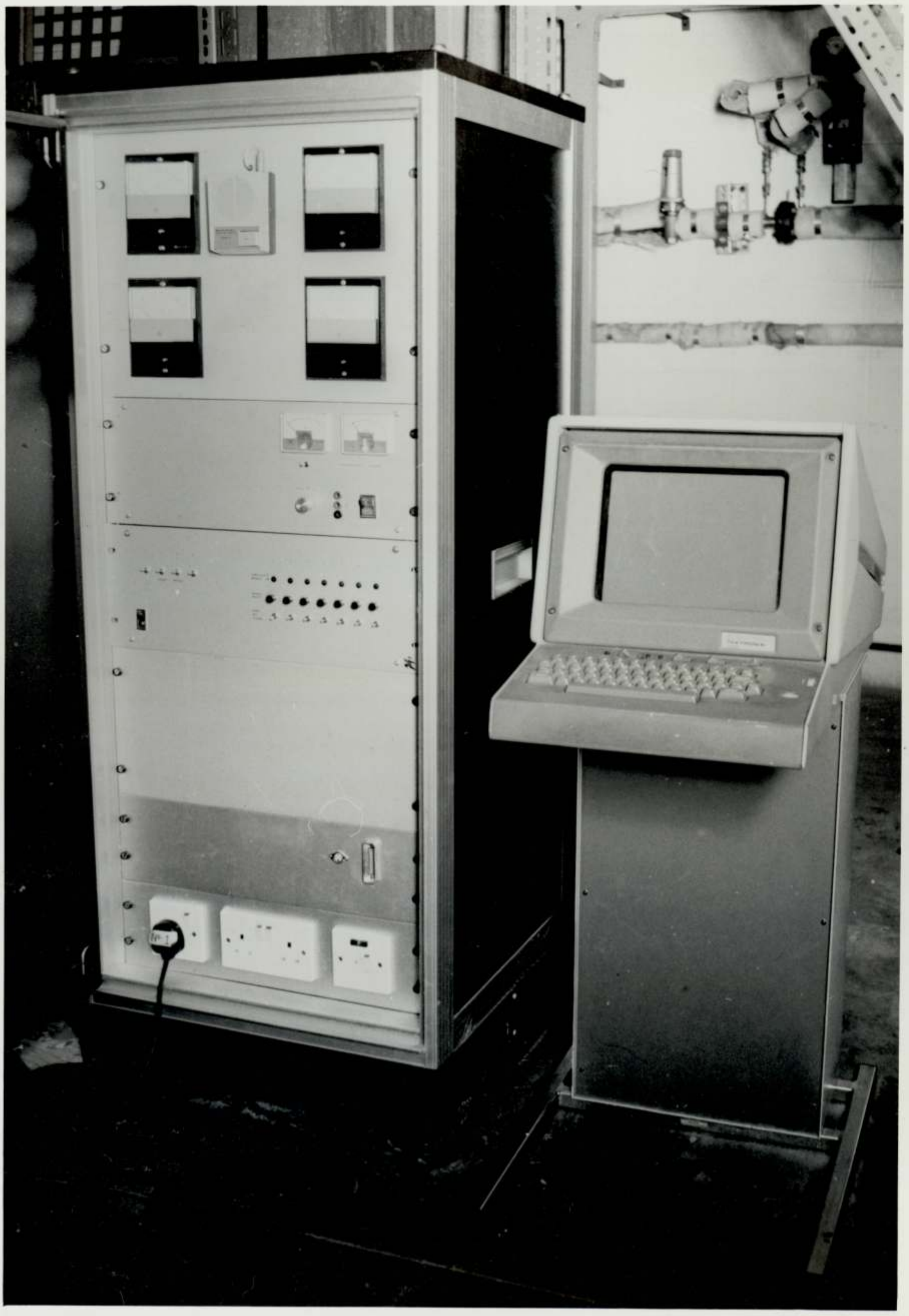
(ix) Mains for V.D.U.

(x) Intercommunicator with the computer room.

Plate 4

A. The V.D.U.
B. Data Conditioning Unit
C. Intercommunictor
D. Flowmeter Indicator
E. Thermocouples Switch
F. Sense Switches
G. Switches for Manual Operation of Valves
H. Socket for H316 Peripherals
I. Switch for HADIOS Unit.





## 5.7 The Honeywell 316 Computer

The Honeywell 316 Computer is designed for real time systems applications as well as batch scientific computation. A wide range of applications can be implemented such as on-line control, data logging and formatting, process monitoring and simulation.
The basic instruction repertoire consists of 72 instructions. These include data transfer, byte manipulation, input/output control and arithmetic operations, as well as a variety of logical, shift, jump and indexing operations. The computer performs most internal operations in 3.2 μs or less. The memory is a random access memory expandable up to 32K words. In the Department at present the memory is 16K words. DAP-16 symbolic assembly program language is used for translation of source programs to machine code. Other source program languages available to the user include FORTRAN and BASIC. The general characteristics of the computer are given in Table 5.5.
The peripheral equipment available include:

(i) A high speed paper tape punch operations at 75 characters per second.

(ii) A magnetic tape cassette unit for input/output (375 bytes per second).

(iii) A high speed paper tape reader operating at 200 characters per second.

(iv) A floppy disc drive.

(v) A teletype operating at 10 characters per second.

(vi) A Textronic 4010-1 visual display unit (VDU) operating at 200 baud.

This unit can easily be moved from the computer room to the pilot plant when needed. The VDU is capable of operating in graphical mode. A hard copy unit is available to provide copies of the display when required.

| | |
|---|---|
| Primary Power | 1 KW at 220V ac ± 15% at 50Hz ± 2Hz. |
| Environment | Room Temperature: 0°C to 45°C |
| Signal Levels | Logical zero: 0v<br>Logical one: 6V |
| Inputs | Diode buffered |
| Cooling | Filtered Forced Air |
| Instruction Complement | 72 Instructions |
| Word Length | 16 bits |
| Memory Cycle Time | 1.6 μs |
| Memory Size | 16K |
| Circuitry | Integrated |
| Addressing | Single address with indexing and indirect addressing. |
| Speed, Add | 3.2 μs |
| Subtract | 3.2 μs |
| Multiply | 8.8 μs |
| Divide | 17.6 μs. max. |

Table 5.5 Honeywell 316 - Characteristics

Plate 5

A. Digital Output Switch
B. HADIOS Cabinet
C. The V.D.U.
D. The Honeywell 316 Computer
E. The HADIOS Switch
F. The Teletype
G. The Paper Tape Reader
H. The Paper Tape Punch
I. The Hard Copy Unit

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# CHAPTER SIX

# THE OPERATION OF THE PILOT PLANT

## 6.1 INTRODUCTION

In this chapter a description of the experimental runs in the pilot plant will be given. The operation of the plant was a sequential exercise in the sense that the procedure for one run is improved by the experience acquired in the previous runs. Therefore, the first three runs were manually operated and an increased amount of automation of the plant was introduced as the experiments proceeded. The possibility of operating the plant both manually or automatically is specially advantageous. In the manual mode of operation the operator is able to interact with the plant at any time, so that in case of equipment instrumentation or computer failure, there is always the possibility of continuing the plant operation. The automatic mode relieves the operator of a large number of duties leaving free time for other type of procedures such as checking measurements, analysing printed data from computer and so on.

The automatic operation of the plant implies the development of software for the communication by the computer with the interface. For that purpose a modified version of the HADIOS Executive Package was used. This is a program written in symbolic assembler language that provides facilities for accessing all the available HADIOS devices from a BASIC program.

Thus, this chapter comprises the following sections:

(i) Operations involved in the manufacture of Formaldehyde Resins,

(ii) The HADIOS Executive.

(iii) The Computer Control of the Pilot Plant.

## 6.2 Operations Involved in the Manufacture of Formaldehyde Resins and in Particular the Butylated Melamine Formaldehyde Resins.

The sequential nature of the operation of the pilot plant and the objective of automation of the 8 hours operation has a decisive influence in the selection of the control strategy. A discussion of the operations involved in the preparation of resins in general, and of butylated melamine formaldehyde resins, in particular follows.

The manufacturing of resins is characterised by a great number of products processed in batch units according to rather similar production methods but different recipes. In general, the process procedure can be divided in the following stages:

1. Metering - the batch process starts by feeding the raw materials from stock to the metering section for recipe dependent metering by quantity meters or weighers. In the pilot plant, this part of the operation is manual since automation is expensive and only justified for large scale plants.
2. Dissolving/Mixing and Charging - The materials are directly fed to the reactor, mixed and dissolved within the reactor. In the case of the manufacture of butylated melamine formaldehyde resins the

formalin is the first raw material to be charged because of the required pH adjustment operation. Butanol is charged next and mixed with formalin by the action of a stirrer of the paddle type installed in the reactor. After this operation the steam to the reactor jacket is initiated, to warm up the mixture so that melamine can be charged and dissolved.

3. Heating and Reaction - After heating to the desired reaction temperature, a catalyst is added. The time at which the catalyst is added is dependent on the raw materials used. In the pilot plant the acid catalyst is added after the water is introduced into the reactor as formalin solution, has been removed. During the reaction period, that may last for several hours, the reactor contents is controlled according to a preselected temperature profile. Since the butylation and to a lesser extent the condensation reaction are negatively influenced by the amount of water present in the reactor, an azeotrope distillation column is needed.

4. Distillation and Separation - These two operations are used in resin plants to remove by-products and reclaim solvents from the reaction mixture. As mentioned earlier, this last stage of the operation is not done in the pilot plant at Aston University. This work is mainly concerned with the third stage of the operation and an appropriate operation procedure is presented in Section 6.2.2.

### 6.2.1 Safety Consideration in the Operation of the Pilot Plant

Safety is a major factor to be considered in any chemical plant dealing with hazardous chemicals. In the manufacture of butylated melamine formaldehyde resins major problems arise from:

1. Flammability of butanol - Flash point of n-butanol is $29^0$C,
2. Toxicity of formaldehyde. The current threshold limit value in force in the United Kingdon is 2 p.p.m. in air. For butanol the value is 50 p.p.m.

In order to avoid any accident the following course of action was followed:

All electricals of the plant were checked out. All the switches were placed in an area well outside the distance recommended by the British Standards Institution publication BS 5345, Part I (1978). The centrifugal pump used to reflux the butanolic phase to the distillation column was surrounded by a metal case with compressed air blown into it. A written operation procedure was approved, involving continuous and undivided attention of the operator. The unwanted solvent is removed from the vicinity of the plant, immediately after being used and taken to the solvent store room. The resin manufactured is discharged to drums, that are labelled and taken to a flameproof area. Proper ventilation is provided by the windows adjacent to the pilot plant and fumes are extracted by a fan with a flexible hose duct that can be directed to any part of the plant. The operator is required to use goggles and gloves when handling formalin or discharging the reactor. Respirators were also provided. In case of skin contact with formalin the area affected is to be washed thoroughly with water. A fire extinguisher was installed near the plant and drop trays fitted underneath each feed tank.

### 6.2.2 Operation Procedure

Reactions change as Table 6.1

| Raw Materials | Quantity |
|---|---|
| Melamine | 12.6 kg |
| 36% Formalin | 44 kg |
| N-Butanol (1) | 33.5 kg |
| N-Butanol (2) | 6.6 kg |
| Xylol | 4.6 l |
| Acid Catalyst | 280 $cm^3$ |

Table 6.1 Reaction Charge for the Experiments in the Pilot Plant

Operation Procedure

1. Clear the area near the pilot plant of all the drums that are not necessary for the batch.

Make sure the window at the top of the pilot plant is open.

2. Switch the mains power on in the data conditioning unit.

3. Switch on the Honeywell 316 Computer and load the HADIOS Executive program.

4. Switch on HADIOS. Switch E on plate No 5 (sec 5.6)

5. Switch on the digital output switch in the HADIOS distribution cabinet. Switch A on plate No. 5 (sec5.6).

6. Bring the Tektronix VDU from the computer room to the plant, and connect it to the plug in data conditioning unit. Switch H on plate No. 4 (sec 5.6).

7. Open the compressed air line, and make sure that all the valves are in working order, by closing and opening them a couple of times using the manual operation and switches.

8. Make sure the feed line to the column, i.e. line connecting reactor to distillation column is open. This line should be always open.

9. Turn the cooling water on.

10. Check levels in the reboiler and decanter.

11. Get some ice from the analytical laboratory and place it in an insulated container to be used as the reference for the thermocouples. Switch the thermocouples on. Plate No. 4 (sec 5.6).

12. Switch on the fan and direct the flexible duct to the top of the reactor where the raw material are to be charged.

13. Before changing the formalin the operator should wear gloves, goggles and the respirator mask.

14. Open the reactor and charge the formalin solution making sure that no dripping occurs. Any spillage should be washed away thoroughly with water.

15. Switch on the stirring system of the reactor.

16. Measure the pH of the formalin and adjust it with 1N NaOH to a pH between 5.6 and 6.0.

17. Change n-butanol (1)

18. Open the compressed air valve to the bottom of the reactor before charging the melamine to prevent it from settling in a dead zone at the bottom of the reactor.

19. Open the steam valve to the reactor and allow five minutes before charging the melamine.

20. Close the reactor and apply full steam to the reactor.

21. Reduce steam flow when the resin temperature reaches $85^{\circ}C$ so that the reactants begin the boil gently at approximately $92^{\circ}C$.

22. Boil gently for 15 minutes and slowly add the xylol.

23. Three hours after boiling add n-butanol (2).

24. When the aqueous phase removed to the tank has reached 30 litres add the acid catalyst.

25. Commence testing for white spirit tolerance and viscosity one hour after the acid addition, and at hourly intervals. If the viscosity rises to a value above 6 -7 PRS add n-butanol to the reactor.

26. When the solvent tolerance reaches a value about 28 mls and below 36 mls switch the steam off.

27. Turn all the motorised valves off.

28. When the resin temperature in the reactor decreases to a value of 60°C, direct the duct of the fan to the bottom valve of the reactor. Wearing gloves, goggles and respirator, discharge the resin into drums that are to be labelled immediately.

29. Remove the drums to the solvent store room.

30. Switch the thermocouples off.

31. Switch off HADIOS, the H 316 Computer and all the peripherals.

32. Switch the mains switch off.

33. Switch the fan off.

## 6.3 The HADIOS Executive

As mentioned before the HADIOS Executive package enables the accessing of all the available HADIOS devices from a BASIC program.

### 6.3.1 Devices Available

(1) Analogue Inputs

48 analogue channels (numbered 0 - 47) are mutliplexed through a common ADC which has an input range of 0-5 V. The converted digital input to the computer is in the range 0-1023, i.e. 10 bit resolution.

(2) Computer Inputs

Three counters are available. Each counter has a range 0-255 and after 255 pulses have been counted returns to zero and resumes counting. The counter can also be programmed to interrupt the computer on reaching a count of 127. In both cases the counters can be preset to an initial (positive) value <255 after each scan or counter interrupt.

(3) Digital Input

Two digital inputs are available. Each has 16 parallel input lines whose values (0 or 1) can be read into the computer.

#### (4) Digital Outputs

Two digital outputs are available. Each has 16 parallel output lines whose values (0 or 1) can be sent out by the computer. The values output remain constant until the next 16 bit word is sent out. Four forms of output are available.

### 6.3.2 Programming Details

All HADIOS input/output is done when subroutine 1 (see below) is first called and thereafter at the end of a time interval selected by the user. The user then communicates with HADIOS by CALL's from his BASIC program as follows:-

```
CALL (1, A(0), B(0))
```

Subroutine 1 is the basic scanning routine. Arrays A (dimensioned 13) and B (dimensioned 120) contain the user parameters and variables.

| | | |
|---|---|---|
| A(0) | Scanning interval | (sec) |
| A(1) | Devices required | |
| | = 1 Analogue inputs | |
| | = 2 Counter 1 | |
| | = 4 Counter 2 | |
| | = 8 Counter 3 | |
| | = 16 Digital input A | |
| | = 32 Digital input B | |
| | = 64 Digital output A | |
| | = 128 Digital output B | |

A(1) should not be set for the digital inputs and digital outputs if only subroutine 5 is used.

The required set of devices is selected by setting:-

| | |
|---|---|
| A(1) | Equal to the sum of the appropriate values above. |
| A(2) | Number of scans required (including the initial scan at time zero) |
| A(3) | First analogue channel |
| A(4) | Last analogue channel |
| A(5) | Number of samples of each analogue channel per scan (ensemble number) |
| A(6) | Counter 1 scan type<br>= 0 no counter interrupt<br>= 1 enable counter interrupt |
| A(7) | Counter 1 preset value |
| A(8) | Counter 2 preset value |
| A(9) | Counter 2 preset value |
| A(10) | Counter 3 scan type |
| A(11) | Counter 3 preset value |
| A(12) | Digital output A mode<br>= 0 from 16 element array at BASIC level (see below)<br>= 1 from subroutine 3 or 4 (see below)<br>= 2 from user supplied subroutine (see below) |
| A(13) | Digital output B mode. |

| | |
|---|---|
| B(0)-B(47) | Analogue input channel reading (each averaged over A(5) samples). |
| B(48) | Counter 1 interrupt time (sec) |
| B(49) | Counter 1 contents at scanning time |
| B(50) | Number of interrupts by Counter 1 during last scanning interval. |
| B(51) | Counter 2 interrupt time (sec) |
| B(52) | Counter 2 contents at scanning time |
| B(53) | Number of interrupts by counter 2 during last scanning interval. |
| B(54) | Counter 3 interrupt time (sec) |
| B(55) | Counter 3 contents at interrupt time |
| B(56) | Number of interrupts by counter 3 during last scanning interval. |
| B(52)-B(72) | Values (0 or 1) read on lists 1 - 16 of digital input A. |
| B(73)-B(88) | Values (0 or 1) read on lists 1 - 16 of digital input B |
| B(89)-B104) | Values (0 or 1) output on lists 1 - 16 of digital output A (when A(12) =0). |
| B(105)-B(120) | Values (0 or 1) output on lists 1 - 16 of digital output B (when A(13) =0) |

CALL (2)

This CALL causes the program to wait for the next clock interrupt (scan time) if all scans requested (A(2)) have not been done - otherwise the BASIC program continues from after the CALL (2).

On a clock interrupt, a scan is performed and the BASIC program continues from after the previous CALL (1, ...) - the inter-scan processing section of the program.

CALL (2) disenables clock and counter(s) interrupt when the scans requested have been done.

CALL (3, D, N, X)

This subroutine provides for a special form of digital output to send out an analogue signal by means of extra hardware when A(12) = 1 or A(13) = 1.

D = 0 digital output A
= 1 digital output B
N = Analogue output channel (1 - 15)
X = Digital equivalent of analogue output for D< X <32 767, the analogue output will be 0 - 10V

CALL (4, D, I, C)

This subroutine controls the format of the digital output when A(12) - 1 or A(13) = 1 as follows:-

D = 0 digital output A
= 1 digital output B
I <0 reset all 16 bits to zero
>0 sets bits 15-2 * I and 16 - 2 * I to value of C leaving other bits unchanged, 0 < I < 7
C = 0 0, 1, 2 or 3 only

This subroutine has been provided to control up to 8 valve devices. Normally, therefore, only 3 values of C will be used (say, 0, 1 and 2).

CALL (5, D, N, X)

D = 1 - position the valve
    2 - read valve position
N = Valve number (0 - 7)
X = Valve position required (D = 1)
    Valve position read (D = 2)
    (Valve scale = 0 - 255)

The subroutine may be called anywhere in the BASIC program. The subroutine assumes that Digital Output A and Digital Input B are assigned to the valves. These devices should not be included in the Devices Required (argument A(1) of subroutine 1).

User Supplied Routine

The user may also supply his own DAP-16 routine to control a digital output device.

The present package contains a dummy version of this routine (called MYSR) which does not cause any output. The user supplied subroutine is called by setting A(12) or A(13). The starting address of the routine should be patched into location '37603 (SPSR). Note that only one of subroutine 3, 4 or the special subroutine may be used for digital output A or B in the same program and at present only one user supplied routine may be added to the package.

In all cases the requested digital output will be performed at the next clock interrupt.

## Further Subroutines

Additional routines may be added to the HADIOS Executive (e.g. for graphics etc.). Such routines must be loaded in sector 35 and below with the base of COMMON (if any) at '35777. There can be 6 routines called from BASIC (numbered 5 to 10). The starting addresses of the routines should be patched into locations '502 onwards and '230 (DAC IBUF) should be patched into '36221 onwards for as many subroutines as can be called from BASIC.

The locations '733 - '777 are available for BASE in sector 0. If more BASE is required it must be located elsewhere (by setting the B register at load time etc.)

## Counter Calculations

The controller rate may be calculated either from the counter interrupt time or from the number of interrupts over a scan interval and the counter contents at the next scan. Thus for counter 1

$$\text{Rate} = (127 - A(7))/B(48)$$

$$\text{or Rate} = ((127 - A(7)) * B(50) + B(49))/A(0)$$

with similar expressions for counters 2 and 3. The latter form is more accurate if the rate is constant over the period A(0) but the former gives an 'instantaneous' rate.

Note that the values of B(48), B(51) and B(54) have no significance at time zero (first scan).

Sense Switch Usage

SS 1 - Normal use for terminating a BASIC program

SS 2 - As for 1 but interrupts are also disenabled (see below)

SS 3 - INPUT statement reads data from tape

SS 4 - PRINT statement writes data to tape

Error Messages

Error Message Format : ERROR XY LINE NNN, where XY is one of the following:

1. TF - The clock interrupt frequency is too small and so BASIC code was still being executed when a clock interrupt took place. This would obviously lead to a backlog of processing at the BASIC level it it were allowed to go unchecked and so execution is terminated.

2. NR - An unidentifiable interrupt has occurred and execution is terminated.

3. NC - The HADIOS controller has interrupted the central processor but the interrupting device was not a counter. Execution is terminated.

4. VI - The execution of the program has been terminated by the user interference this is caused by setting sense switch 2. When interrupt is ocurring it is preferable to terminate execution in this way

rather than by setting sense switch 1 as the setting of sense switch 2 causes all interrupts to be disenabled.

5. RI - A real to integer conversion error has occurred in the HADIOS Executive, i.e. conversion of a real number outside the range -32768 to +32768 was attempted.

6. SE - User supplied subroutine has been called (A(12) or A(13) = 2) but is not loaded.

## 6.4 The Computer Control of the Pilot Plant

The traditional methods of control of chemical processes and particularly distillation columns, rely on model independent feedback forms of control. They have provided acceptable control of the plants despite little knowledge of the dynamic characteristics of the plants (128). It involves selecting a set of measurement variables which when controlled at a given value (set point) make the plant operate in the desired way and according to the safety requirements. These variables are controlled by a collection of single loop controllers which act on another set of variables, the manipulated variables that hopefully make the plant return to the required operation state. The manipulated variables should be easily adjustable and flow rates are often used. Modification to single loop concept such as cascade, feedforward, ratio are made when necessary. The adjustment of the feedback controller gains is made during the start up of the plant by trial and error to achieve adequate performance. This approach relies heavily on past experience of the operator and is adequate for pilot plant control systems. The simplicity of the single loop approach brings many advantages for the operator and it is handily analysed for linear design technique (127).

The methodology used for the operation of the pilot plant was to run the plant, initially, in manual mode an, as the experiments proceeded to introduce an increase amount of automation as the operator became more familiar with the operation of the plant. The single loop approach is particularly suitable for this kind of methodology and has provided the background and experience for more elaborate model dependent control schemes.

### 6.4.1 The Control Arrangement of the Pilot Plant

Figure 6.1 depicts the control loops used in the pilot plant. Four loops were implemented:

1. Two interactive loops for the level control of the interface and top layer of the decanter. The manipulated variables are the water offtake rate and reflux to column.
2. A level control of the reboiler. The manipulated variable is the bottom flowrate.
3. A cascade loop for the temperature control in the reboiler. The manipulated variable is the heat input rate to the reboiler.

The control objective can be stated as follows: To run the plant in such a manner so that the resin properties in the reactor meet the pre-established specification. The sequential nature of the process and its operation procedure lead to another operation implemented by the computer. As the batch proceeds

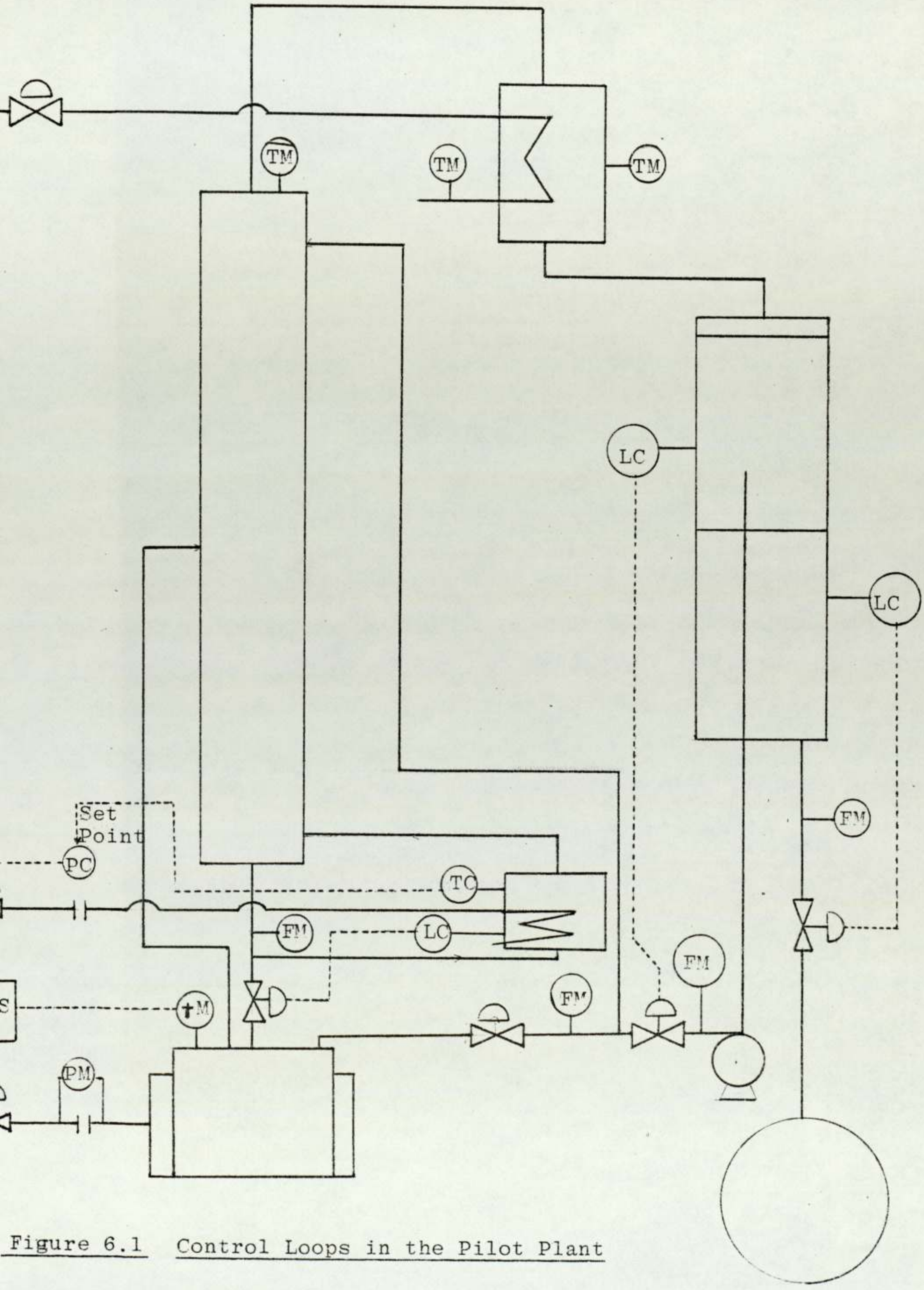


Figure 6.1 Control Loops in the Pilot Plant

and the reactor charge gets drier, i.e. less water present due to its removal from the plant the temperature in the reactor increases. In order to keep the feed rate to the column at an acceptable level more steam is necessary to supply the reactor as the batch proceeds. Based on that knowledge and on past experience another loop was programmed that related the temperature in the reactor with the amount of steam supplied to that same unit. That is represented in Figure 6.1. with the designation of temperature sequential control.

### 6.4.2 Direct - Digital Control (DDC) Algorithm for 3-Term Control.

To implement a 3-term control requires that the connecting element for the controlled process condition be provided with a signal v, which consists of terms proportional to the deviation $\theta$, proportional to the time integral of the deviation and proportional to the time derivative, i.e. the rate of change, of the deviation. The deviation is the difference between the measured value of the controlled condition $\theta_o$ and the set value $\theta_i$; $\theta = \theta_o - \theta_i$. For completeness of the expression for v, a constant $v_s$ must be included. Thus:

$$v = v_s + k_1 \theta + k_2 \int \theta dt + k_3 \frac{d\theta}{dt} \qquad (1)$$

The constants $k_1$, $k_2$ and $k_3$ are, respectively, the proportional, integral and derivative action factors. Normally the equation above is written in the form

$$v = v_s + k_1 \left(\theta + \frac{1}{T_I} \int \theta \, dt + T_D \frac{d\theta}{dt}\right) \qquad (2)$$

where $T_I$ is the integral-action time and $T_D$ the derivation action time.

The equation given above is the one that an analogous type controller will follow to implement 3-term control. For a digital computer to perform the equivalent control requires that the measured value of the controlled condition be sampled at its entry to the computer.

A further sampling procedure is necessary at the output from the computer where there is conversion of the signal to analogue form and where a storage device maintains this analogue between the sampling instants. It is this value which is applied to the process as a connecting signal between the two points at which sampling occurs, the computer must perform a control algorithm. Equation (2) may be converted to a difference equation. Using the Simpson rule for the numerical representation of the integral we can write for the n sampling time:

$$v_n = v_s + k_1 \left( \theta_n + \frac{\tau}{3T_I} \sum_{k=0}^{n} (\theta_k + 4\theta_{k-1} + \theta_{k-2}) + \frac{T_D}{\tau} (\theta_n - \theta_{n-1}) \right) \quad (4)$$

$$v_{n-1} = v_s + k_1 \left( \theta_{n-1} + \frac{\tau}{3T_I} \sum_{k=0}^{n-1} (\theta_k + \theta_{k-1} + \theta_{k-2}) + \frac{T_D}{\tau} (\theta_{n-1} - \theta_{n-2}) \right) \quad (5)$$

Subtracting (5) from (4) and making $\Delta v_n = v_n - v_{n-1}$, we can write

$$\Delta v_n = v_1 \left( (\theta_n - \theta_{n-1}) + \frac{\tau}{3T_I} (\theta_n + 4\theta_{n-1} + \theta_{n-2}) \right.$$

$$\left. + \frac{T_D}{\tau} (\theta_n - 2\theta_{n-1} + \theta_{n-2}) \right) \quad (6)$$

or

$$\Delta v_n = A\,\theta_n + B\theta_{n-1} + C\theta_{n-2} \quad (7)$$

where

$$A = k_1 \left( 1 + \frac{\tau}{3T_I} + \frac{T_D}{\tau} \right) \quad (8)$$

$$B = k_1 \left(\frac{4}{3T_I} - \frac{2T_D}{\tau} - 1\right) \tag{9}$$

$$C = k_1 \left(\frac{\tau}{3T_I} + \frac{T_D}{\tau}\right) \tag{10}$$

Equation (7), (8), (9) and (10) were used in the computer program to implement the controllers.

### 6.4.3 The Computer Program for the Control of the Pilot Plant

Following the strategy explained in sec. 6.4.1 and using a two term controller , i.e. proportional and integral actions, a computer program was written, which, by means of HADIOS and HADIOS Executive, implements the control of the pilot plants. The computer program is next presented.

#### 6.4.3.1 The Motorised Valves

The valves installed in the plant can be driven automatically by a signal from the computer and also manually by action of the appropriate switches in the remote signal conditioning unit. Since complete shut off is not the real function of the motorised valves, and because it can be difficult to achieve, each motorised valve is preceeded by a diaphragm valve that can close the line when needed. Two different problems may arise during the operation of the motorised valves.Electrical

```
10  DIM E(4),G(4),J(4)
5  DIM Q(4)
0  DIM S(3)
0  DIM U(4),V(4),Z(4)
0  DIM K(4)
5  DIM M(4)
0  DIM A(13)
0  DIM B(120)
2  L=.89
3  FOR I=0 TO 4
5  M(I)=100
8  NEXT I
9  M(3)=10
0  FOR I=0 TO 13
0  A(I)=0
00  NEXT I
10  FOR I=0 TO 120
20  B(I)=0
30  NEXT I
35  X5=100
37  X9=140
40  A(0)=10
50  A(1)=17
60  A(2)=3600
70  A(3)=0
80  A(4)=14
90  A(5)=5
91  CALL (5,1,6,X5)
92  CALL (5,2,6,X6)
93  CALL (5,2,6,X6)
94  IF X5=X6 GOTO 200
95  GOTO 191
00  T=-A(0)
05  T9=240/A(0)+.1
10  FOR I=0 TO 4
20  READ K(I),R(I)
30  NEXT I
40  DATA 5,1000,10,1000,.2,1000,1,.1E06,32,1000
50  FOR I=0 TO 4
60  U(I)=K(I)*(1+A(0)/(3*R(I)))
70  V(T)=K(I)*(4*A(0)/(3*R(T)-1))
80  Z(I)=K(T)*(A(0)/(3*R(I)))
85  NEXT I
90  FOR I=0 TO 3
00  READ S(I)
10  NEXT I
20  DATA 30,12,900,115
30  FOR I=0 TO 4
40  G(I)=0
50  J(I)=0
60  NEXT I
70  I=0
75  C=31
80  CALL (1,A(0),B(0))
81  GOTO 1500
```

```
82  CALL (5,1,7,X9)
90  T=T+A(0)
00  REM                    LOOP 0 WATER OFF TAKE
10  H=9.52/(1-L)-31.5*L/(1-L)+25*B(6)/(1023*(1-L))+9.84
20  E(I)=H-S(I)
25  I=0
30  M(I)=M(I)+U(I)*E(I)+V(I)*G(I)+Z(I)*J(I)
35  X=M(I)
40  GOTO 1000
45  M(I)=X
50  CALL (5,1,4,X)
55  Q(I)=G(I)
60  G(I)=E(I)
70  J(I)=Q(I)
80  IF C<T9 GOTO 540
90  F=B(0)/1023*60
00  PRINT T
05  PRINT X6
07  CALL (5,2,7,X8)
08  CALL (5,2,7,X8)
09  PRINT X8
10  PRINT F
20  PRINT H
30  PRINT M(I)
40  REM                    LOOP 1 BUTANOL REFLUX
50  I=I+1
60  H1=197.21+40*B(5)/(1023*L)-25*B(6)/(1023*L*(1-L))
70  E(I)=H1-S(I)
80  M(I)=M(I)+U(I)*E(I)+V(I)*G(I)+Z(I)*J(I)
85  X=M(I)
90  GOTO 1000
95  M(I)=X
00  CALL (5,1,3,X)
05  Q(I)=G(I)
10  G(I)=E(I)
20  J(I)=Q(I)
30  F1=B(1)/1023*60
40  IF C<T9 GOTO 680
50  PRINT F1
60  PRINT H1
70  PRINT M(I)
80  REM                    LOOP 2 LEVEL IN REBOILER
90  I=I+1
00  E(I)=B(8)-S(I)
10  M(I)=M(I)+U(I)*E(I)+V(I)*G(I)+Z(I)*J(I)
15  X=M(I)
20  GOTO 1000
25  M(I)=X
30  CALL (5,1,1,X)
35  Q(I)=G(I)
40  G(I)=E(I)
50  J(I)=Q(I)
60  IF C<T9 GOTO 802
70  F2=B(3)/1023*60
80  PRINT F2
90  PRINT B(8)
800  PRINT M(I)
802  REM                    LOOP 3 TEMP. OF REBOILER
803  I=I+1
804  T2=.12*B(14)
805  E(I)=S(I)-T2
806  M(I)=M(I)+U(I)*E(I)+V(I)*G(I)+Z(I)*J(I)
807  IF M(I)>25 THEN M(I)=25
808  IF M(I)<0 THEN M(I)=0
809  I=I+1
810  E(I)=M(I-1)-B(7)*25/1023
811  M()=M(I)+U(I)*E(I)+V(I)*G(I)+Z(I)*J(I)
812  IF M(I)<0 THEN M(I)=0
```

```
3   IF M(I)>250 THEN M(I)=250
4   X=M(I)
5   CALL (5,1,5,X)
6   Q(I)=G(I)
7   G(I)=E(I)
8   J(I)=Q(I)
20  P=B(7)*25/1023
22  IF C<T9 GOTO 851
23  PRINT M(I-1)
24  PRINT P
25  CALL (5,2,5,X7)
26  CALL (5,2,5,X7)
27  PINT X7
28  PRINT M(I)
29  PRINT T2
30  REM                          OTHER MEAS. OF INTEREST
32  REM                          T3 TEMP. IN REACTOR
34  REM                          TEMP. AT COLUMNS TOP
36  REM                          TEMP. IN DECANTER
38  REM                          PRES. DROP REACTRS STEAM LINE
39  PRINT S(3)
40  T3=.121*B(13)
41  GOTO 1700
42  T4=.119*B(11)
43  CALL (5,1,7,X9)
44  T5=.119*B(10)
45  T6=.12*B(12)
46  P1=B(9)*25/1023
47  PRINT T4
48  PRINT T3
49  PRINT T5
50  PRINT T6
51  IF C>24 THEN C=1
52  C=C+1
54  I=0
56  CALL (2)
58  STOP
60  END
000  IF X>160 THEN X=160
010  IF X<60 THEN X=60
020  X1=INT(X)
030  X2=X1/2
040  X3=INT(X2)
050  IF X3=X2 THEN 1080
060  X=X1-1
070  GOTO 1090
080  X=X1
090  IF I=0 THEN 445
100  IF I=1 THEN 595
110  IF I=2 THEN 725
500  IF B(57)=0 GOTO 1530
510  IF B(58)=1 GOTO 1550
520  S(3)=111
525  GOTO 390
530  IF B(58)=1 GOTO 1570
535  S(3)=115
540  GOTO 390
550  S(3)=117
560  GOTO 390
570  S(3)=113
580  GOTO 390
700  I T3>97.5 GOTO 1730
710  X9=140
720  GOTO 842
730  IF T3>100 GOTO 1760
740  X9=170
750  GOTO 842
760  IF T3>110 GOTO 1790
```

```
 770  X9=200
 780  GOTO 842
 790  X9=250
 800  GOTO 842
2000  IF X>250 THEN X=20
2010  IF X<6 THEN X=6
2020  X=INT(X)
2030  GOTO 813
```

striction may occur, i.e., the valve does not respond to small changes in the input voltage. This problem can solved by software by calling twice the subroutine number 5 (see program sec 6.4.3). Mechanical striction is the second problem that can only be solved by proper maintenance and cleaning of the valves each time the pilot plant is operated.

Two different types of control valves were used in the pilot plant: electrical valves for the steam and cooling water lines and pneumatic valves for the other lines. The signals from HADIOS to the valves have 8 bit resolution (0 to $256_8$). The signal to the electrical valves was made to vary from 6, totally closed, to 250 totally open position, by programming (instructions 2000 to 2030). For the pneumatic valves, and due to the characteristics of the actuator the range was narrowed from 60 corresponding to a pressure of 3 psi to 160 for a pressure of 15 psi. This can be seen in the program from instructions 1000 to 1110.

### 6.4.3.2 The Level Measurements in the Decanter

For the implementation of the level controller in the decanter, it is necessary to relate the height of liquid of each phase with the measurement signal from HADIOS. Channel 6 and channel 7, corresponding respectively to B(5) and B(6) signals from HADIOS, were selected for each pressure cell. The installation is the pressure cells is different Each pressure cell has two fittings corresponding to a high pressure and low pressure switch outlets. The high pressure top of channel 6 was connected to the decanter and the low pressure outlet was left in contact with the atmosphere. For channel 7 the high pressure tap is connected to a wet leg filled with water (31.5 in) and the low pressure outlet is linked to the decanter. Figure 6.2a shows the dimensions of the decanter, and Figure 6.2b the connections of the pressure cells and decanter.

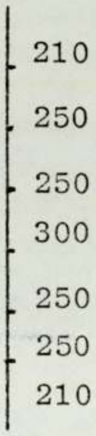


Figure 6.2a

Decanter Height (in mm)

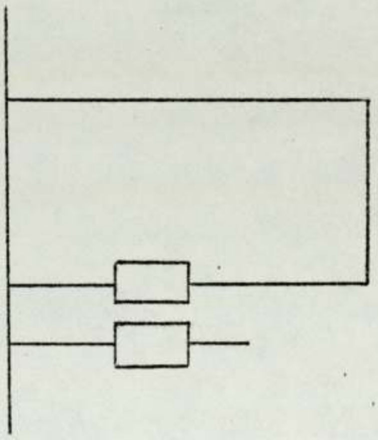


Figure 6.2b

Connections of Pressure Cells and Decanter.

Channel 6 - Range 20 - 60 in of water

20 in = 508 mm 0 volt

60 in = 1524 mm 5 volt

Taking as reference the level of channel 6 and keeping in mind that B(5) is a digital signal with 10 bit resolution the following equation can be written

$$\frac{B(5)}{1023} = (\Delta P - 20)/40$$

where $\Delta P$ is the differential pressure in in. of water.

$$\Delta P = \frac{40\ B(5)}{1023} + 20 \qquad (11)$$

But, $\Delta P = h_w + h_B \times L$ (12)

Where, $h_w$ is the height of water phase in the decanter, $h_B$ is the height of alcoholic phase in the decanter and L its density. From (11) and (12),

$$h_w + h_B\ L = \frac{40\ B(5)}{1023} + 20 \qquad (13)$$

Channel 7 - Reverse range, according to Figure 6.3. Full scale 25 in of water.

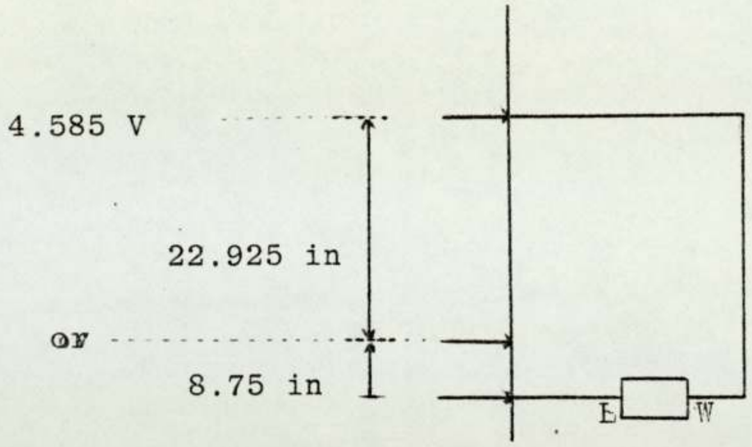


Figure 6.3 Measurement Signals for Channel 7.

To relate the digital signal from the computer, B(6), with the low pressure tap, the following equation can be written,

$$\frac{B(6)}{1023} = \frac{22.925 - (31.5 - P_L)}{25} \qquad (14)$$

where $P_L$ is the pressure at the low pressure tap. Rearranging,

$$P_L = 8.575 + \frac{25\ B(6)}{1023} \qquad (15)$$

To relate $P_L$ with the height of water and wet butanol, $h_w$ and $h_B$ it must be noticed that the same reference line for channel 6 and 7 must be considered. The difference between the two levels of both channels is 250 mm or 9.842 in.

Therefore,

$$P_L = (h_w - 9.842) + L\ (31.5 - (h_w - 9.342)) \qquad (16)$$

Considering that the overall level of liquid in the decanter is above the top tap of channel 7, and interface above lower tap of channel 7.

$$P_L = (1 - L)\ (h_w - 9.842) + 31.5\ L \qquad (17)$$

From (15) and (17),

$$h_w = \frac{8.575}{(1-L)} - \frac{31.5\ L}{(1-L)} + \frac{25\ (B(6)}{1023(1-L)} - 9.8425 \qquad (18)$$

From (13) and (17)

$$h_B = \frac{31.5}{(1-L)} + \frac{1}{L}\ [10.1573 - \frac{8.573}{(1-L)} + \frac{40\ B(5)}{1023}$$

$$- \frac{25\ B(6)}{1023\ (1-L)}\ ] \qquad (19)$$

Equation (18) and (19) relate the heights of aqueous and alcoholic phases in the decanter with the digital signal from HADIOS. They are based on the manufacturers calibration and the dimensions of the decanter as given in the Q.V.F. manufacturer's catalogue. Since the aqueous phase was considered to have density 1, and the dimensions of the decanter were not very accurate, several bench experiments were done to verify the equations. Therefore, equations (18) and (19) suffered slight changes for better fitting of the experimental results.

Bench Experiment

Wet butanol density =.889

Set point

$h_w$ = 125 + 250 + 150 mm = 525 mm

= 20.7 in of water

$h_B$ = 150 + 250 = 650 mm

= 25.6 in of butanolic phase

Computer readings

B(5) = 636.3

B(6) = 806.1

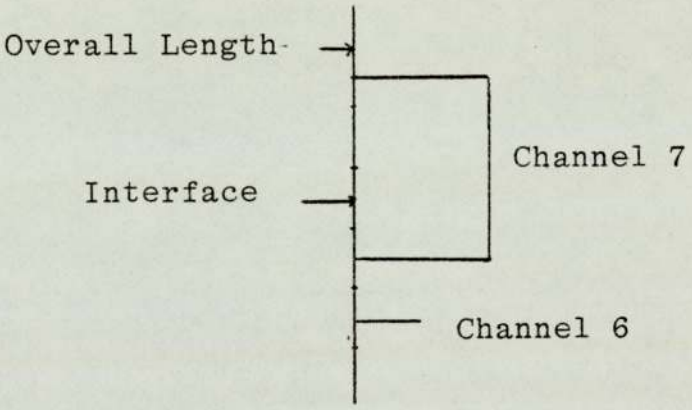


Figure 6.4 Typical Bench Experiment

Using equation (3) and the experimental results,

20.7 + .889 x 25.6 + 40 (636.3)/1023

$\therefore$ x = 18.64

In this case equation (3) was rewritten as,

$$h_w + L\ h_B = 18.64 = 40\ B(5)/1023 \qquad (20)$$

Doing the same for equation (18).

$$h_w = \frac{9.52}{(1-L)} - \frac{31.5\ L}{(1-L)} + \frac{25\ B(6)}{1023\ (1-L)} + 9.84 \qquad (21)$$

From (2) and (21)

$$h_B = 197.21 + \frac{40\ B(5)}{1023\ L} - \frac{25\ B(6)}{1023\ L\ (1-L)} \qquad (22)$$

Equations (21) and (22) were used in the control program (see section 6.4.3).

The calibration of thermocouples and the equations used in the program are derived in Appendix 5.

# CHAPTER SEVEN

# EXPERIMENTAL RESULTS AND CONCLUSIONS

## 7 INTRODUCTION

In this chapter, the experiments done on the pilot plant at Aston University will be described, and the results analysed and discussed. Six complete runs of the pilot plant were done together with other experiments, necessary for the testing, calibration and tuning of controllers of the plant. These "bench" experiments which did sometimes last for several hours were carried out using butanol and water as raw materials. The proportion of butanol and water used were the same as the ones used in a "real" run of the resin manufacture, but formalin was not present.

The objective of the experiments were twofold:

(1) To operate the plant and get familiar with the process at a pilot plant level in order to identify process variables and conditions that influence the manufacture of butylated formaldehyde resins.

(2) From the information and experience acquired during the successive batches, to implement and improve, in a sequential manner, the control of the plant.

### 7.1 Description of the Experiments - Log Sheets

Most of the history of the experiments done is summarized in table A.6.1 to table A.6.5 (App. 6). The first run was not completed due to the danger of gelation of the resin in the reactor. Therefore, no log sheet is presented. The following additional remarks must be made about the experiments:

Run No. 1 - Operation was completely manual. When formalin was charged it was noticed that a considerable amount of formaldehyde had precipitated and settled at the bottom of the container. The formalin used in this case, was transported from BIP to Aston University one week before the experiment took place. It was stored in an unheated room where temperatures at night dropped noticeably. This fact lead to the precipitation of formaldehyde from the formalin solution, which in turn occasioned a series of problems during the batch. When formalin was charged in the reactor, the bottom valve of the reactor was blocked due to the accummulation of precipitate at the bottom of the reactor. Since, underneath the stirrer there is a non mixed zone, the precipitate settled there and the discharge area of the reactor was clogged. To overcome this problem in future batches it was decided to connect the compressed air line to the bottom of the reactor, just above the discharge valve, so that blockage of the valve could be prevented.

When the first sample of the resin was taken, it was noted that it presented a yellow colour and undissolved products were present making it appear hazy. The solvent tolerance was negligible and the viscosity high ( 10 PRS). In order to prevent gelation of the resin inside the reactor some butanol was added and the plant shut off immediately.

<u>Run No. 2</u> - Was initiated with fresh raw material and formalin was transported from BIP to Aston University on the day of the experiment. No computer control was implemented but the analogue inputs to the computer were tested. The thermocouple in the reboiler was found to be defective and was replaced later for future experiments. The operation was carried out over two days, and due to a slow increase in solvent tolerance, 8 litres of butanol were added in the latter stages of the batch. Immediately after, a sudden increase in white spirit tolerance was noticed, and the upper limit of solvent tolerance of the resin specification was exceeded.

<u>Run No. 3</u> - The thermocouple in the reboiler was replaced and found to be in working order. Batch on manual, smooth increase in white spirit tolerance and viscosity constant in the second stage of the batch. No extra butanol added.

Run No.4 - First experiment in which computer control was used. Level controller in decanter working well, but difficulty in controlling the temperature in the reboiler during the first part of the batch. A build up of liquid in the column at that stage with the pressure reading in the reboiler, causing the level in the reboiler to decrease. Due to the decrease in transfer area the reboiler heat input rate decreases and the temperature in the reboiler decreases too. In this situation the steam to the reactor had to be decreased to diminish the liquid hold up in the column. In the second stage of the batch the temperature loop was returned and the variation of temperature in the reboiler was much improved. A power cut occurred in the middle of the run. Extra 7 kg of butanol were added to the resin to improve solvent tolerance.

Run No.5 - Computer controlled batch with cascade temperature control loop. Digital input 8 was used for changing the set point of the temperature loop. The following sequence was used:

B(57) = 0 and B(58) = 1 T set = 113
B(57) = 0 and B(58) = 0 T set = 115
B(57) = 1 and B(58) = 1 T set = 117
B(58) = 1 and B(58) = 0 T set = 119
See program sec. 6.3 (instruction 1500 to 1580).

Improvement of the temperature control loop.

Some extra acid catalyst was used.

Resin within the specification.

Run No. 6 - Sequential temperature control in the reactor implemented according to:

If $T$ reactor $\leqslant 97.6^{\circ}C$ Valve postion in the reactor steam line = 140

$97.5 < T$ reactor $\leqslant 100^{\circ}C$ Valve position in the reactor steam line = 170

$100 < T$ reactor $\leqslant 110^{\circ}C$ Valve position in the reactor line = 250 (fully open)

$110^{\circ} > T$ reactor Valve position in the reactor line = 250 (fully open)

See program sec. 6.3 (instruction 1700 to 1800)

Extra 1 gallon of butanol was added to the resin to improve solvent tolerance.

## 7.2 RESULTS AND DISCUSSION

Figure 7.1 illustrates the rate of aqueous phase removal during the operation of the plant. The results are consistent for the five runs, and the amount of aqueous phase removed at the end of each batch varies from 39 litres for batch No. 4 to 40.5 for batch No. 2. The power cut in the middle of Run No. 4 is shown in Figure 7.1 by a decrease in the aqueous phase removal rate for $.375 < T < .5$. Due to this external factor the amount of water removed at the end of the batch is slightly less the corresponding amount for other runs. It is also noticeable from the figure that the last two runs (Runs 5 and 6) present a much smoother and continuous variation of the water removal rate when compared to the previous batches. That is due to the improved operation of plant as a consequence of better control of the plant.

Figure 7.2 depicts the variation of the reactor temperature during the runs. It is obvious from the graphs that a common pattern exists for all the cases. The temperature of the reactor at the beginning of the batch changes very slowly for about two hours due to the composition of the reaction mixture. At that time the reactor contains a considerable amount of water and the composition of the vapour leaving the reactor is very close to the azeotropic composition. In the next stage of the process and after the butanol (2) and acid addition, the increase in temperature is very sharp and the temperature rises from approximately 97°C to 115°C in approximately 3 hours. This stage corresponds to the period in which some aqueous phase is being removed but at a smaller rate than in the initial stages of the process. The comparison of the mixture inside the reactor changes drastically during this period. The final two hours of the process correspond to a level of the curves both in Figure 7.1 and Figure 7.2. Some variations from run to run are apparent in Figure 7.2 and it can be attributed to small variations in the composition of the raw materials. Run No. 2 and No. 4 show a later transition from stage 1 to stage 2, i.e. the sharp variation of temperature in the reactor appeared after the acid catalyst addition. For Run No. 4 that can be explained by the power supply failure, whereas for Run No. 2 it has to be attributed to the operator's action since the run was done in manual mode.

Figure 7.3 shows the variation of viscosity in the different runs. In spite of all the runs being able to reach the required specification it is very clear that the viscosity of the resin in Run No. 2 and No. 4 varies much more than any other run. In terms of the reactions taking place, this means that at the later stages of the process, the condensation reaction is too fast at the expense of the butylation reaction (slower increase in white spirit tolerance). If no action was taken (addition of "dry" butanol) the final product of these runs would probably be outside the specification range due to over condensation. Figure 7.4 illustrates the variation of white spirit tolerance of the resin with time. The two runs in which no extra butanol was added to the resin, show a steady increase in solvent tolerance during the four hours of the second stage of the reaction. It is significant to observe that the two lines have equal slopes. Runs No. 6 started with a low tolerance, due to the low temperatures in this batch, but the rate of increase of the property is remarkably high and comparable with Run No. 3 and No. 5. When extra butanol was added the solvent tolerance increased at a higher rate and the product specification was met after four hours of operation in the second stage. Again Run No. 2 and No. 4 present anomalous behaviour that could be detected after the second sample of the resin because of the low rate of increase in solvent tolerance. Butanol addition has proved to be an effective way to promote the solvent tolerance of the resin.

Figure 7.5 shows the levels in the decanter over a period of time in a typical computer controlled batch. As can be seen the levels are maintained constant and small variations from the set points are due to noise at the measurement level. Figure 7.6 represents the reboiler variation and the corresponding variation of valve position (heat input) of the reboiler steam line.

Figure 7.1 Aqueous Distillate removal vs fractional time.

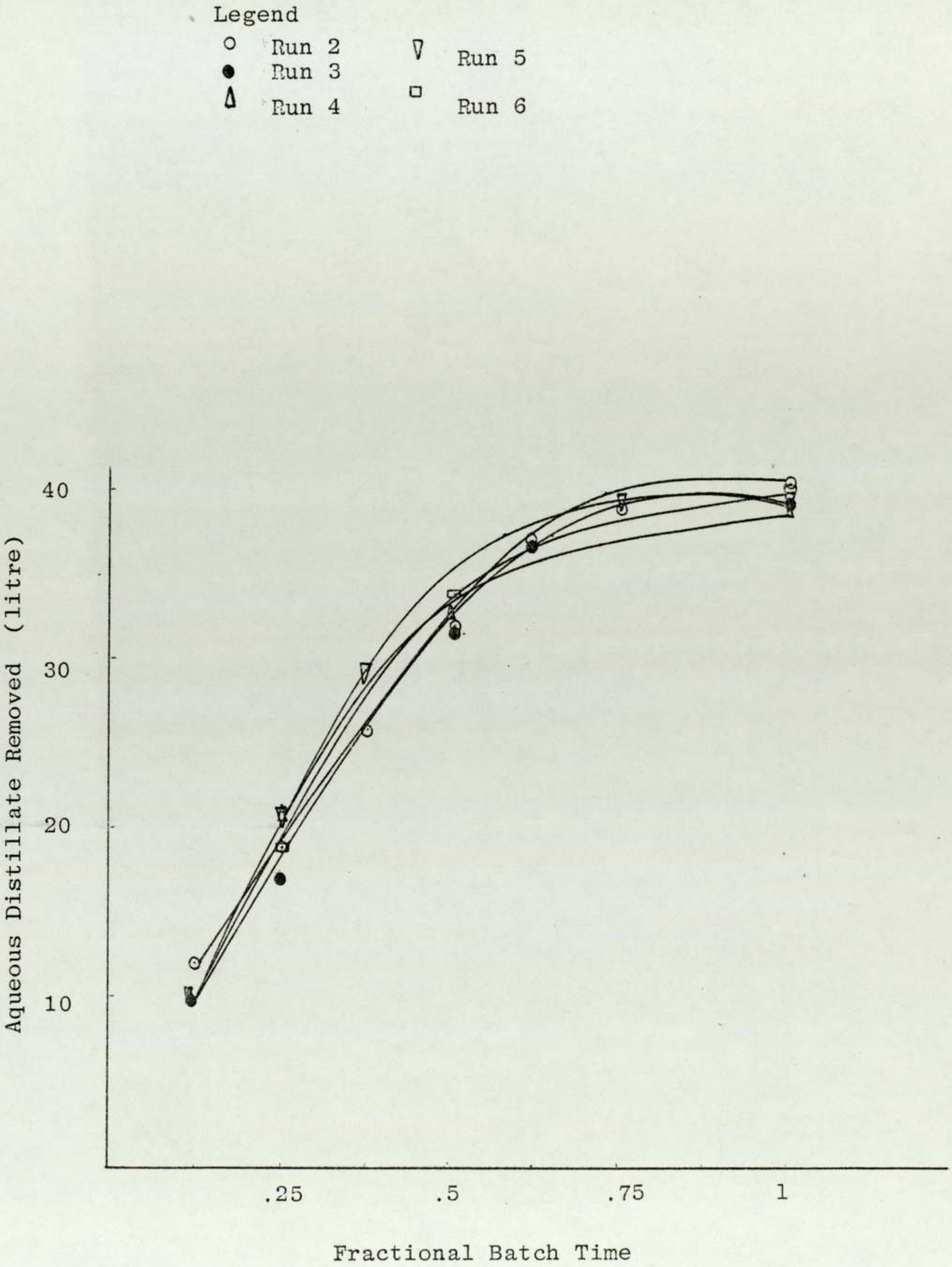
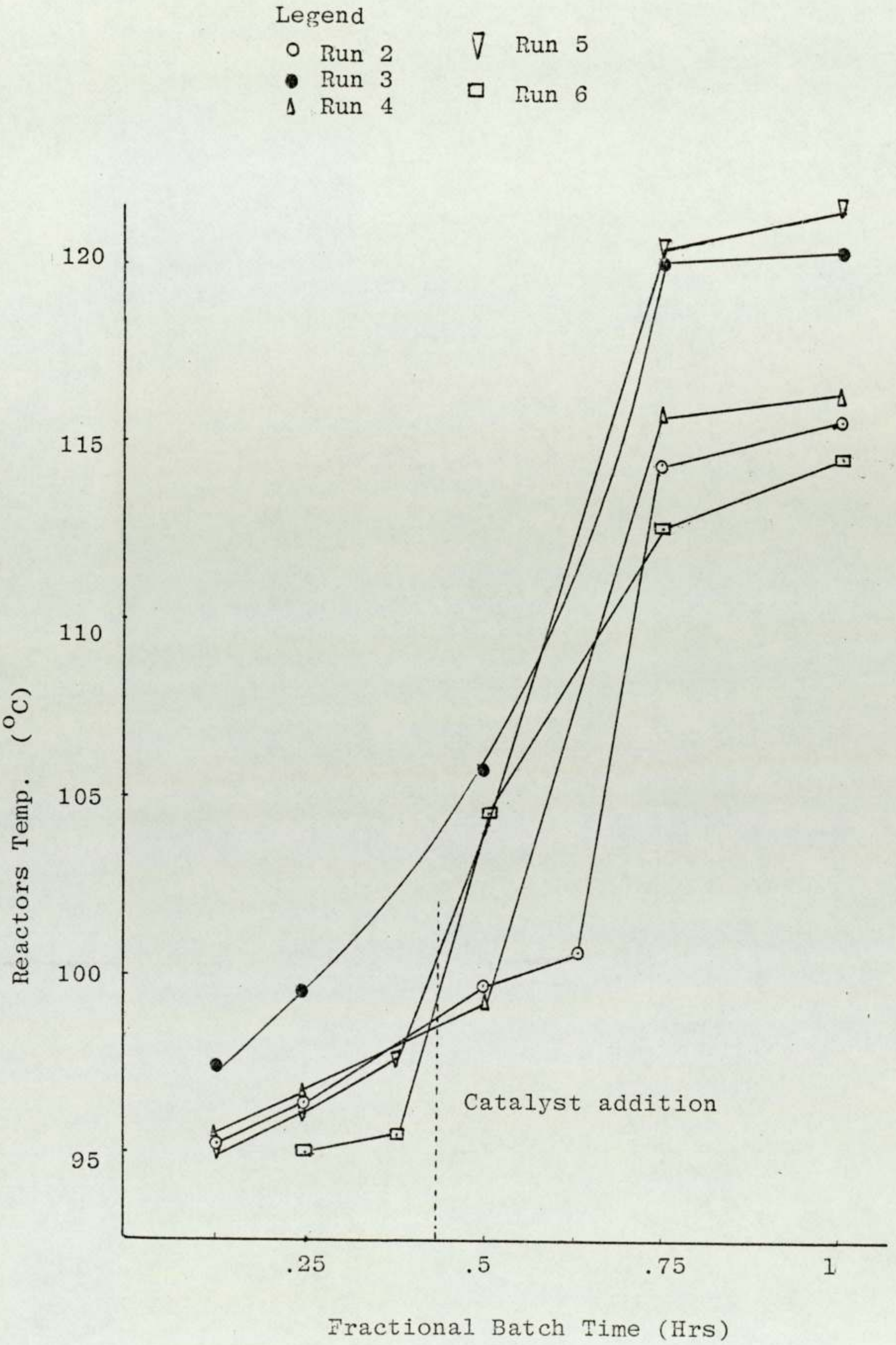


Figure 7.2 Reaction Temperature vs Fractional Batch Time



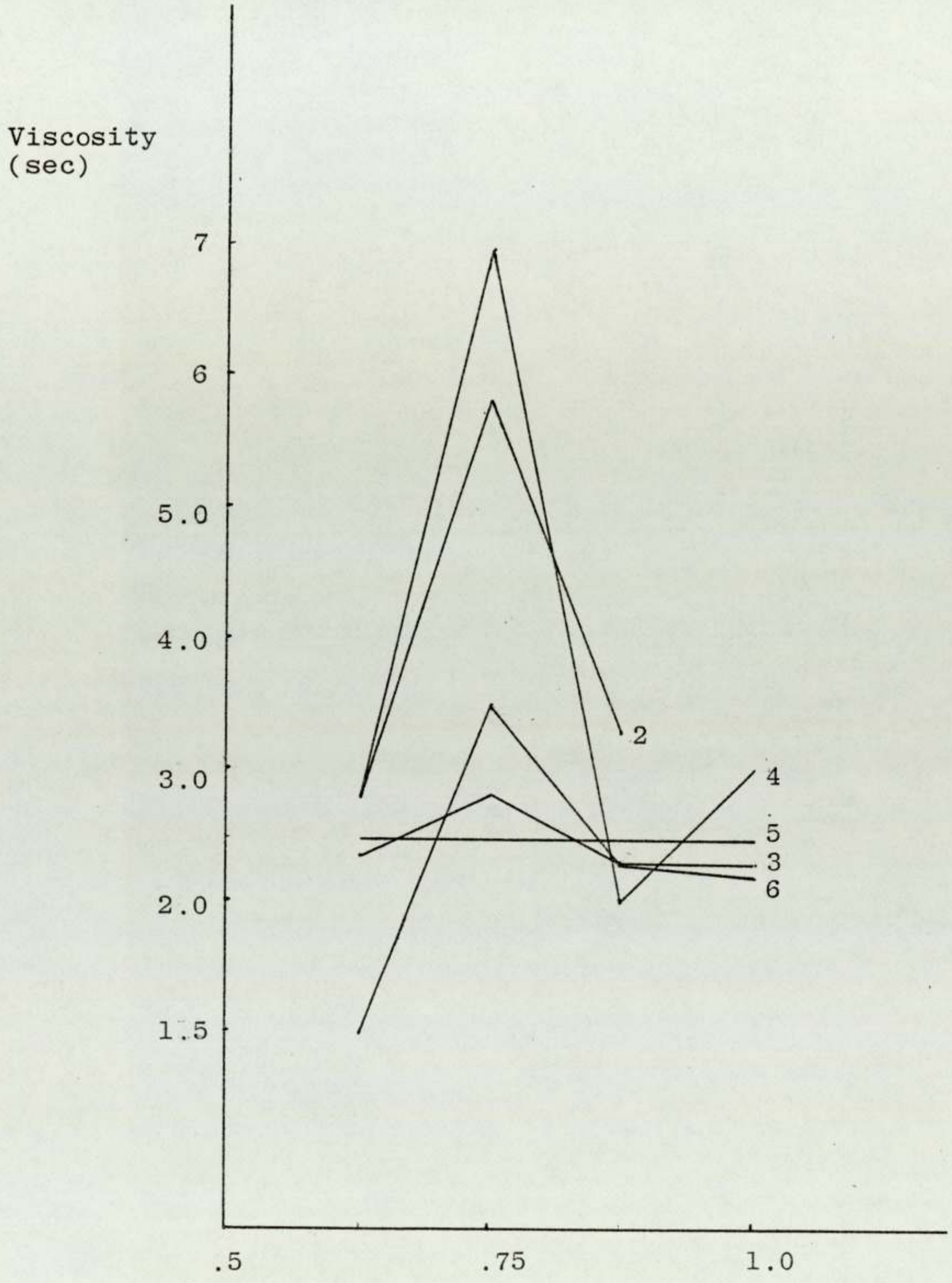


Figure 7.3 Viscosity vs Fractional Batch Time

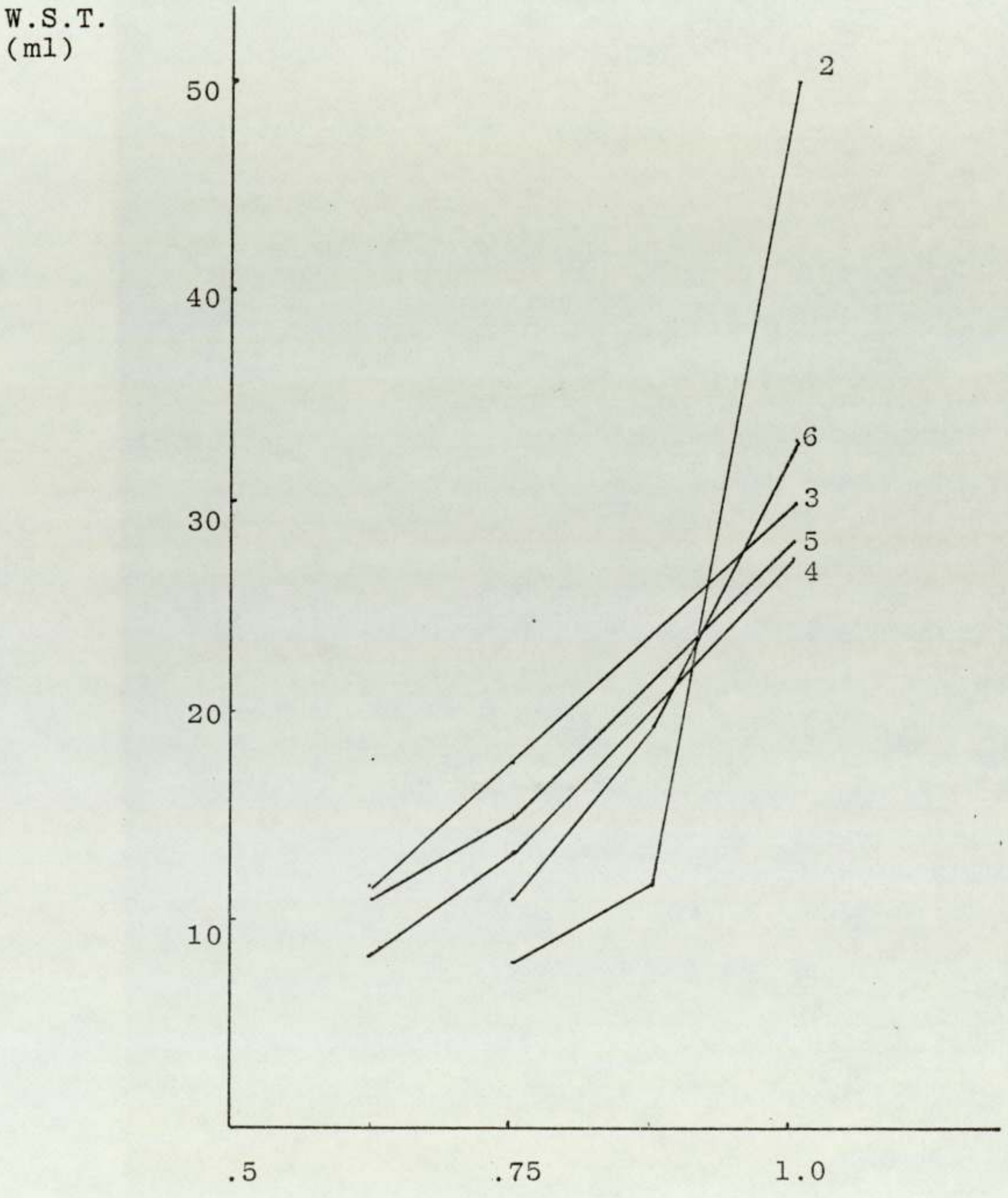
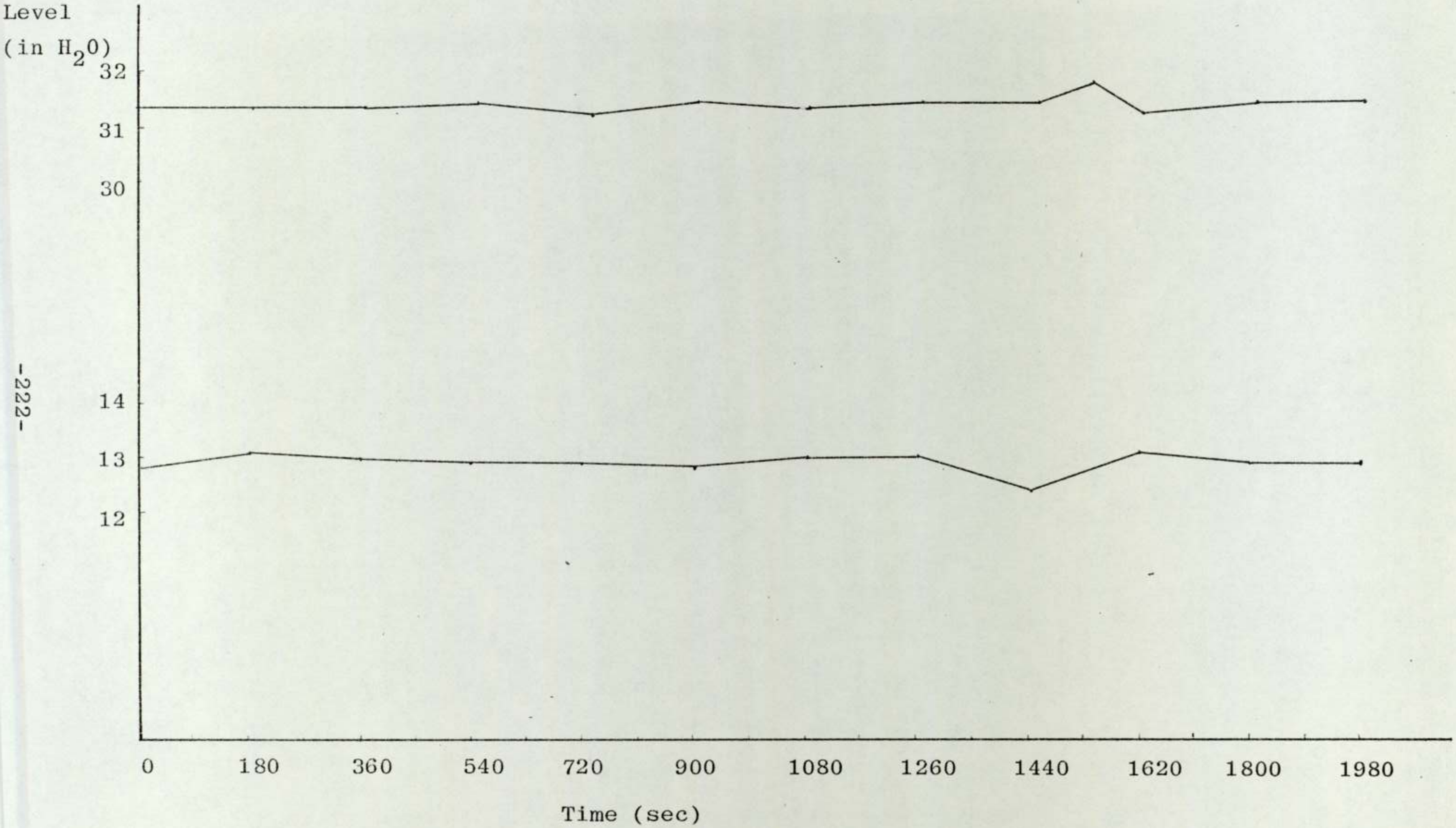
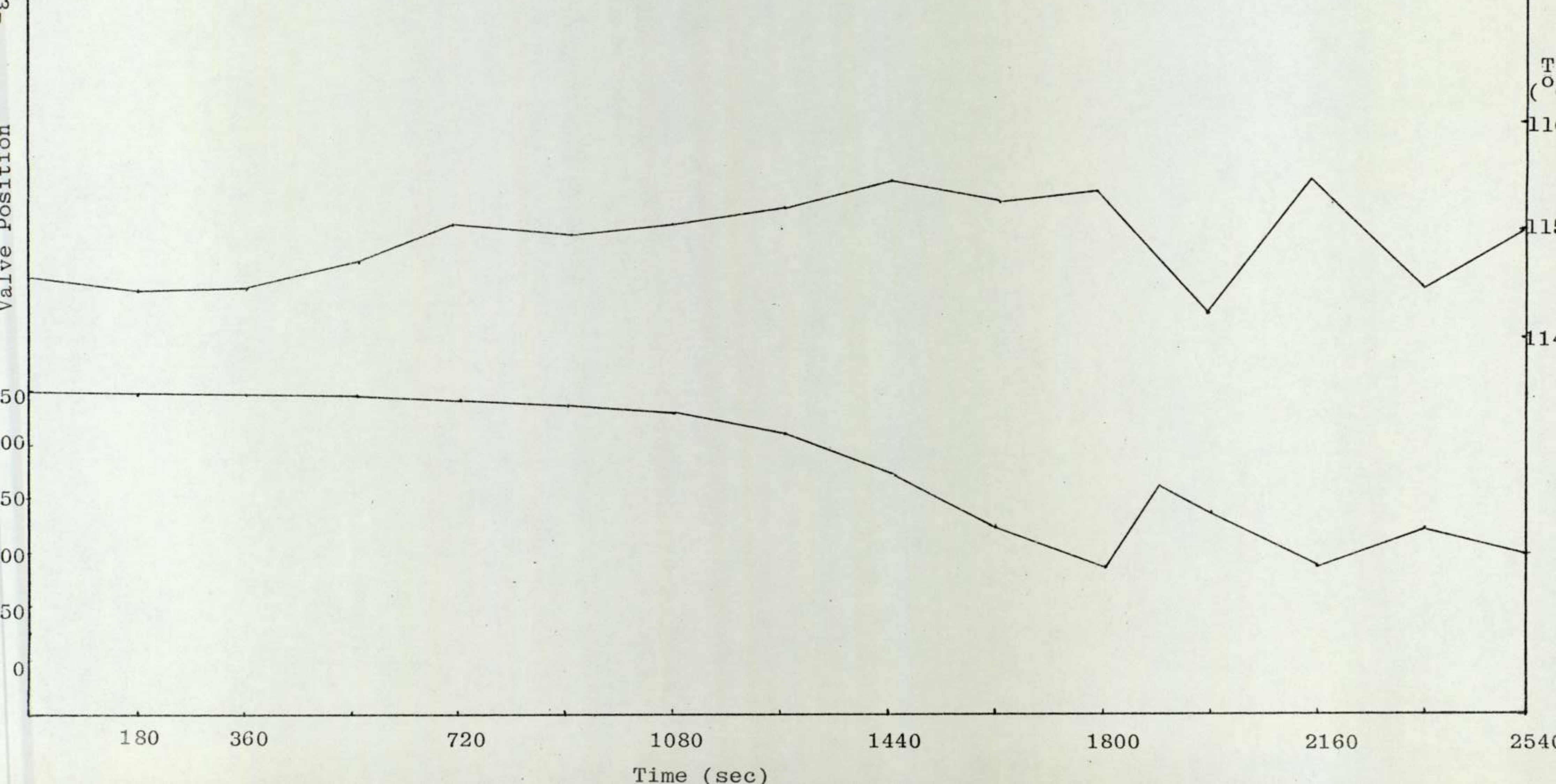


Figure 7.4 White spirit tolerance vs batch time.

Figure 7.5 Levels in decanter vs time



valve position vs. time.



The temperature loop control of the reboiler was found more difficult to control than any other variable in the process. Shinskey (129) studied the control of azeotropic distillation processes and has shown that boilup must be set in proportion to feed rate and composition according the eq. 1

$$\frac{V}{F} \qquad \frac{Z(X_D - W)}{X_D(y - W)} \qquad (1)$$

where,

$V$ = boilup rate

$F$ = feed to the column

$Z$ = composition of the feed to column (water mole fraction)

$X_D$ = composition of the aqueous distillate

$W$ = composition of the bottom product

$y$ = composition of the top vapour.

The value of $X_D$ is fixed by the temperature at which the decanter is operating and W is fixed by the set point of the temperature in the reboiler. Therefore, it can be said that V/F is to be adjusted according to the values of Z and y. In the case of the pilot plant Z is constantly changing as is shown by the variation of the temperature in the reboiler. If the composition at the top of the column, y, is to remain constant, a constant variation of V/F is necessary.

The sequential temperature control of the reactor as implemented by the computer program in sec. 6.3 changes the feed to the column according to a preselected sequence based on the experience of the operator. The heat input to the reactor increases along the batch by opening the valve of the steam to the reactor. This approach, requires the attention of the operator to check the temperatures of the reboiler and top of the column, to make sure that the correct V/F ratio is achieved.

For a better control of the temperature in the reboiler it is necessary to rely on model based control schemes.

## 7.3 CONCLUSIONS

The raw materials quality, especially the formalin condition is a major factor in the manufacture of butylated melamine formaldehyde resins. In order to obtain a product well inside the specification the right amount of formaldehyde must be used. Run No. 1 is an example of how a poor quality formalin compromise the success of a batch. The experimental results of A. Firth, (see Chapter 4), also show that a low charge of formaldehyde leads to an over condensated product. The importance of this factor in the manufacture of M:F resins is further stressed by the lack of product sample in the first stage of the process (before the acid catalyst addition). In fact, since the first sample of the resin is only taken about five hours after the start of the batch, at this stage of the process it is too late to take an effective corrective action to bring back the product to specification. The rate of change in solvent tolerance of the resin between Sample 1 and Sample 2 gives a clear indication of the progress of the two main reactions.

Any corrective action on the product must take into account this property together with the viscosity changes taking place. The addition of extra butanol has a clear effect on the improvement of the white spirit tolerance of the resin. This action should only be taken when the rate of increase of a white spirit tolerance (W.S.T.)

between Sample 1 and Sample 2 is low. The correct rate of increase of W.S.T. for the case of the pilot plant was found to be 5-6 ml/hour. The process time in the pilot plant at Aston was consistently 8 hours for the computer controlled batches with the second stage of the operation lasting for 4 hours. This represents an improvement when compared with operation times in industry. The distillation system used in the pilot plant (reflux to the top of the column) is more effective in removing the water from the reactor, especially at the latter stage of the process when the water in the reactor is low. The formaldehyde:melamine ratio in the reactor's initial charge has a clear influence on the kind of bridge formed during the first stage of reaction. The proportion of methylene-ether bridges formed at this stage is clearly favoured by high formaldehyde:melamine ratios. Low F:M ratios, like the case of M:F = 4.5 (see chapter 4), do not show the typical decrease in molecular weight after the acid catalyst addition.

The computer control of the plant brings a clear improvement of the operation of the plant. The operating conditions are much more consistent throughout the operation and that brings an improvement in the product quality. The amount of information on the operational variables and the operation of the plant in control mode gives the operator the opportunity to monitor the process much more closely and therefore take the right corrective actions whenever necessary.

The temperature of the reaction mixture and/or the amount of aqueous phase removed from the process and two operation variables that give a clear measurement of the progress of the batch.

The temperature of the decanter, was found to have no appreciable influence in the operation provided it remains between 10 and 30°C.

# CHAPTER EIGHT

# FURTHER WORK

## 8 INTRODUCTION

In the present work one of the major objectives was to construct a pilot plant for the manufacture of butylated melamine formaldehyde resins at Aston University. The plant was interfaced with the Departmental Honeywell 316 Computer and the automatic control of the plant was implemented. This work being part of a broader research program, it is important to remember that there is plenty of room for improvement in the process in various different areas. These last few pages are concerned with the suggestions for further work in the areas of the project where the author feels that work should be continued.

### 8.1 Kinetic Model

Two different approaches can be taken for the improvement of the kinetic model. A deterministic model, like the one presented in this thesis, and a stochastic model based on the reactivity of the groups involved in the reaction. In the first approach the following variables should be included in the model. Temperature of the reaction mixture and pH of the reaction medium. As mentioned in Chapter 2 no thermodynamical and kinetic information exists in the open literature for the conditions of the industrial production of butylated melamine formaldehyde resins.

In order to improve the model and include these two variables in the simulation program, it is felt that further experimental work in the chemistry of the melamine formaldehyde resins is needed. In that work, conditions similar to the ones encountered in industry (mixed aqueous) butanolic medium and temperatures ranging from 90 to 120° C should be used.

The second approach is a totally different way of analysing the reactions taking place. The functional groups intervening in the reaction used to collide in in order to form a new chemical bond. The collision of the molecules is a random process but the probability of a new bond being formed by the collision of two functional groups depends on the groups themselves Making use of a random number generation subroutine available in most computer systems software, and giving different "weights" to each functional group to describe its reactivity a flexible stochastic model of the reaction can be established. This approach was used by Ishido (130) to simulate the phenol resins reaction system. In this approach, experimental work is also necessary to establish the reactivity of each functional group.

Closely related to the problem of getting reliable information about the chemistry of M:F resins, is the problem of the availability of chemical and instrumental methods of analysis. Further research is also necessary in this field, especially to clarify the nature of the condensation bridges formed during the process and determine the effect of operation conditions in the chemical structure of the product.

## 8.2 Plant

The following course of action is thought to improve the plant operation:

(1) To fix a feed line connecting the reactor directly with the condenser. In the first stage of the process when considerable amounts of water are present in the reactor, it is useful to study the effect of directing the feed of the reactor to the condenser and use the butanolic top phase as feed to the column. This arrangement would provide a constant composition feed to the column (provided the temperature of the decanter is constant) and would simplify the start-up of the plant. At the later stages of the process the present arrangement of the distillation column is more effective since the feed from the reactor is drier than the butanolic phase in the decanter.

2. To replace the electrical valves in the steam lines to the reboiler and condenser. The present valves introduce considerable time delays in the control loops since it takes two minutes for the valve to travel from the totally open to the totally closed position.

3. To provide means of automatic measurement of viscosity of the resin in the reactor. The viscosity has proved to be a useful property for the characterisation of the product. It is therefore thought to be desirable to have an automatic measurement of viscosity as replacement of the off line tests of resin viscosity that are time consuming (20 minutes) and inaccurate. The problem of selecting measurement properties for the characterisation of the resin chemical structure and therefore its specification is another field of research that needs to be considered. Some work has been done on phenol-formaldehyde resins by Volckek,(131), using automatic refractive index measurements to characterise the resins properties. The search for a suitable measurement for this purpose is important so that the chemistry of the process can be closely related to the process operation.

## 8.3 Control of the Operation of the Plant

The single loop approach to the control of the operation of the plant is one of the many possible approaches for the control of the plant. More sophisticated forms of control should be tried to take full advantage of the computer capability and techniques for decoupling the interaction between the loops (modal control) are thought to be useful routes of improving the control of the process.

# APPENDIX ONE

## QUALITY CONTROL TESTS

## 1. Standard Method of Test for Viscosity - 25°C - P.R.S.

Apparatus

1. A set of Standard Paint Research Station Bubble Viscometers including the A standards.
2. Standard P.R.S. Viscosity tubes.
3. Thermostatically controlled water bath at 25°C.

Procedure

A PRS viscosity tube should be filled to the mark with resin solution and placed in the water bath at 25°C ± 0.5°C for at least thirty minutes. The viscosity shall be determined by comparing the bubble travel, after inversion of the tube, with P.R.S. standards under the same conditions.

## 2. Solvent Compatibility at 20°C

Apparatus

Balance - towers type
250 ml beaker - tall form
Thermometer - 10° to 110°C
Burette - 50 ml x 0.1 ml divisions
Standard newsprint.

Procedure

Weigh 5 g resin into the 250 ml beaker. Add the appropriate solvent from the burette, mix well with the thermometer and continue the additions until the newsprint placed beneath the beaker just cannot be read.

The solvent may be added in fairly large increments up to 2/3 of the minimum expected volume, and thereafter in reduced quantities until the end point is reached.

The successive solvent additions must be small enough to prevent precipitation within the mixture, and the temperature must be maintained at 20°C throughout the test.

### 3. Solid Resin Yield at 120°C

Apparatus

A ventilated oven provided with a fan and maintained at
120 ± 2°C as measured at any point within the oven.
Flat bottomed tinplate dish 7 cms diameter and 1 cm deep.
Watch glass
Desiccator (containing silica gel)
Analytical balance capable of weighing to 1 mg.

Procedure

The clean tinplate dish shall be dried for at least 30 minutes in the oven at 120°C and after washing in the desiccator, weighed to the nearest milligram (W1).

2.0 ± 0.1 g of the sample is weighed into the dish and the sample weight recorded to the nearest milligram (W2). 2.0 mls of 3° xylene (BS 458-1) are added from a pipette. The tinplate dish is then covered with a watch glass and allowed to stand for 10 minutes.

After removing the watch glass, the dish and contents shall be placed on a perforated sheet metal shelf and put into the oven which shall be maintained at 120°C ± 2°C throughout the determination.

After two hours, the dish shall be removed from the oven, allowed to cool in the desiccator and re-weighed (W3).

$$\text{Solid Resin Yield } \% = \frac{W3 - W1}{W2} \times 100$$

Record the average results of duplicate determinations which should not differ by more than 1.0%

4. Acid Value

Apparatus

Balance - capable of weighing to 0.1g - towers type

Beaker - 100 mls capacity

Glass stirring rod

Burrette 25 ml subdivided 0.05 mls

Measuring cylinder - 50 ml.

Reagents

Titration solvent. Mix together equal volumes of acetone; 740 P Industrial methylated spirit and 3°C xylene. Render the mixture neutral to alkali blue solution.

Alkali Blue indicator solution - Dissolve 0.1 g Alkali Blue in 100 mls of Industrial methylated spirit. Normal aqueous solution of sodium hydroxide - standardised and decinormal solution of sodium hydroxide - standardised.

Procedure

Using the towers type balance, weigh out 28g of resin into a 100 ml beaker. Add 50 ml of ti titration solvent and dissolve the resin using a glass rod for agitation.

Titrate the resin/solvent mixture with sodium hydroxide solution employing 1 ml of alkali blue solution as indicator (colour change from blue to pink). Stir the mixture continously throughout the titration.

Acid value - mg KOH/g resin solution = $t \frac{56.1}{28} \times N1$

where t = titration in mls

and N1 = normality of sodium hydroxide solution used.

# APPENDIX TWO

## ANALYTICAL METHODS FOR THE DETERMINATION OF FUNCTIONAL GROUPS OF THE RESIN MOLECULE.

## 1. Determination of Free Formaldehyde

### Reagents

2M Sodium Sulphite Solution

N/1 Sulphuric Acid

N/1 Sodium Hydroxide

Thymolphthalein (0.1% in alcohol)

### Method

Weigh accurately by difference from a weighing bottle between 2 and 3 grams of resin into a 500 ml conical flask containing 200 mls distilled water. The solution is agitated to disperse the resin, then carefully neutralised with N/1 NaOH to thymolphthalein.

Add 10 mls $H_2SO_4$ from a burette followed by 25 mls neutral sodium sulphite solution. Allow to stand for 1 minute then back titrate the excess $H_2SO_4$ with N/1 NaOH using thymolphthalein as indicator.

Carry out the determination in duplicate.

### Calculation

$$Na_2SO_4 + CH_2O\ (aq) + H_2O \rightarrow HO\ CH_2\ NaSO_3 + NaOH$$

30 grams $CH_2O \equiv$ 1000 mls N/1 NaOH

$$\%\ \text{Free } CH_2O = \frac{(10-t) \times 0.03}{W} \times 100$$

W = weight of sample (grams)

t = vol. of N/1 NaOH required to neutralise the excess $H_2SO_4$

## 2. Determination of Nitrogen

The determination of nitrogen is done in B.I.P. by the standard Kjeldahl method according to the procedure indicated by BELCHER (60).

## 3. Determination of Butoxy Groups

Zeisel method is used with a 2-hour boiling process and allowing the condenser water to boil towards the end (60).

## 4. Determination of Total Formaldehyde

Total formaldehyde is determined by distillation from aqueous phosphoric acid at 110$^{\circ}$, followed by iodometry, (1).

# APPENDIX THREE

## LOG-SHEETS OF LABORATORY EXPERIMENTS

| Time | Temperature °C | | Dist-illate $cm^3$ | Observations |
|---|---|---|---|---|
| | Resin | Head | | |
| 9.00 | | | | pH formation 3.65 - 5.7 with $1cm^3$<br>N/1 NaOH<br>Melamine + Butanol (1) charges |
| 9.20 | | | | Heat on (2.5) |
| 9.40 | 60 | | | Heat up (3.5) |
| 9.45 | 70 | | | Heat up (4.0) |
| 9.48 | 78 | | | Resin clear |
| 9.52 | 90 | | | Reflux. Heat down. |
| 10.05 | 94 | 88 | | Addition of xylol. Heat up (3). Distilling. |
| 10.20 | 93 | 88 | ~10 | Xylol addition complete |
| 11.05 | 92 | 88 | 88 | |
| 11.35 | 93 | 88 | 125 | Heat up (3.5) |
| 12.05 | 93 | 90 | 185 | |
| 13.20 | 93 | 90 | 350 | Heat down (3) + Butanol (2). |
| 13.35 | 94 | 90 | 362 | Butanol (2) addition complete. |
| 14.05 | 94 | 90 | 415 | Heat down (2.3) Stirrer slower. |
| 14.35 | 95 | 90 | 463 | |
| 15.00 | 96 | 90 | 500 | |
| 15.40 | 98 | 90 | 560 | Heat off - Addition of catalyst.<br>Heat on. |
| 16.00 | 100 | 90 | 615 | Heat off. |
| 9.45 | | | | Heat on |
| 10.07 | 99 | 90 | 615 | Distilling. |
| 10.45 | 109 | 90.5 | 675 | |
| 11.05 | 115 | 98 | 700 | Heat down (2.5). Stirrer slow. |
| 11.20 | 117 | 96 | 705 | Heat off. Sample 1.<br>PRS 4-4A WST = 15.5 $cm^3$<br>Paraformaldehyde in aqueous distillate. |

| Time | Temperature °C |  | Dist-illate $cm^3$ | Observations |
|---|---|---|---|---|
|  | Resin | Head |  |  |
| 11.45 | 120 | 96 | 710 | Addition of 3.4 $cm^3$ catalyst. |
| 13.30 | 122 | 97 | 730 | Sample 2 PRS 5A<br>WST-38.3 |
| 14.15 | 122 | 93 | 735 | Heat off |
| 15.50 | 70 |  |  | Vacuum 25" Heat on (2.5) |
| 15.58 | 70 | 61 |  | Distilling |
| 16.10 | 75 | 66 |  | Heat off. PRS $13A^-$ + 40 $cm^3$ of distillate.<br>142 g distillate |

Final Resin Properties

PRS - $12A^+$

Solids yield - 63.7%

Solvent Tolerance - 43 mls

Acid Value - 0.32 mg KOH 1 g

Log Sheet No. 1 - Progress of the first laboratory experiment.

| Time | Temperature °C | | Distillate cm$^3$ | Observations |
|---|---|---|---|---|
| | Resin | Head | | |
| 9.15 | | | | pH formation 3.6-6 (1 cm$^3$ NaOH)<br>Melamine + butanol (1) changed. |
| 9.30 | 30 | 20 | | Heat on (8) |
| 10.00 | 92 | | | Reflux. Heat down (1) |
| 10.15 | 90 | | | Addition of xylol. Heat up (7). |
| 10.20 | 92 | 88 | | Distilling |
| 10.28 | 91 | 88 | 10 | Xylol addition complete |
| 10.45 | 91 | 88 | 40 | |
| 11.15 | 91 | 88 | 85 | |
| 11.45 | 91 | 88 | 140 | |
| 12.15 | 91 | 88 | 185 | Heat up (7.5) |
| 13.20 | 91 | 89 | 330 | Heat down (5.8) |
| 13.30 | 91 | 89 | 340 | Addition of butanol (2) |
| 14.15 | 92 | 90 | 400 | |
| 14.45 | 91 | 90 | 445 | Heat up (7.5) |
| 15.15 | 92 | 90 | 510 | |
| 15.40 | 92 | 88 | 560 | Addition of catalyst (7.6 cm$^3$) |
| 16.15 | 98 | 91 | 640 | |
| 16.30 | 102 | 93 | 660 | Heat off |
| 8.30 | | | | Heat on (7) |
| 9.00 | 104 | 86 | | Distilling |
| 9.30 | 110 | 92 | 680 | |
| 10.00 | 113 | 96 | 698 | Heat down (6). Stirrer slow. |
| 10.30 | 120 | 96 | 705 | Sample 1. Heat off.<br>PRS $3^+$ WST 29.3 |
| 11.30 | 120 | 95 | 715 | Sample 2. Heat off.<br>PRS $4^-$ WST 45.8 |
| 13.20 | | | | Vacuum 25 mmHg. Heat on |
| 14.05 | 63°C | 48°C | | |
| 14.30 | 70 | | | Sample 3. PRS $14^-$+80cm$^3$ distillate - PRS $12^-$<br>180 grams of distillate. |

Final Resin Properties

PRS - $11A^-$

Solids - 63.2%

W.S.T. - 43.3 ml

Acid Value - 0.48 KOH/g

Log Sheet No. 2 - Progress of second laboratory experiment.

# APPENDIX FOUR

## PHYSICAL CHARACTERISTICS OF THE EQUIPMENT

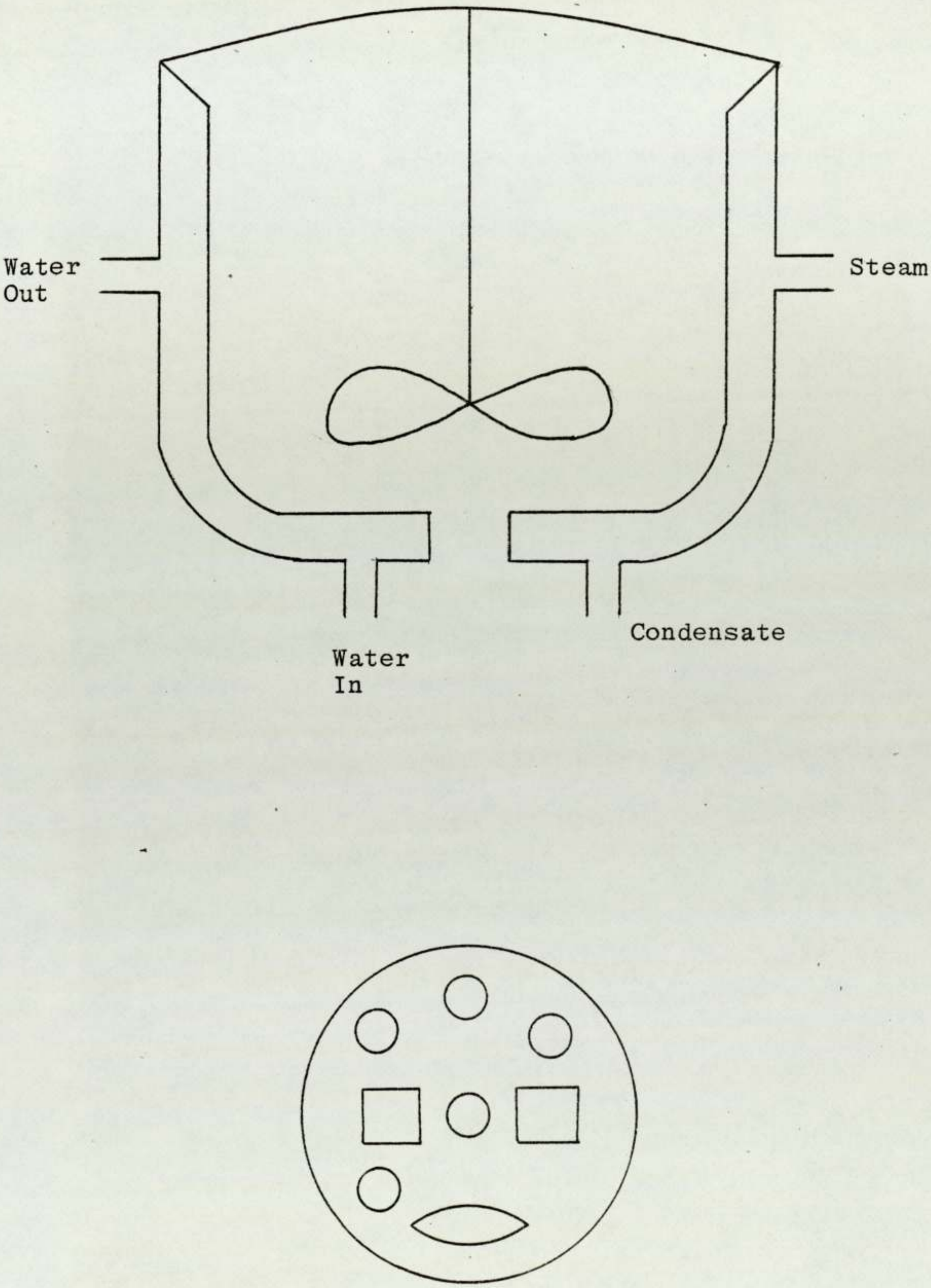
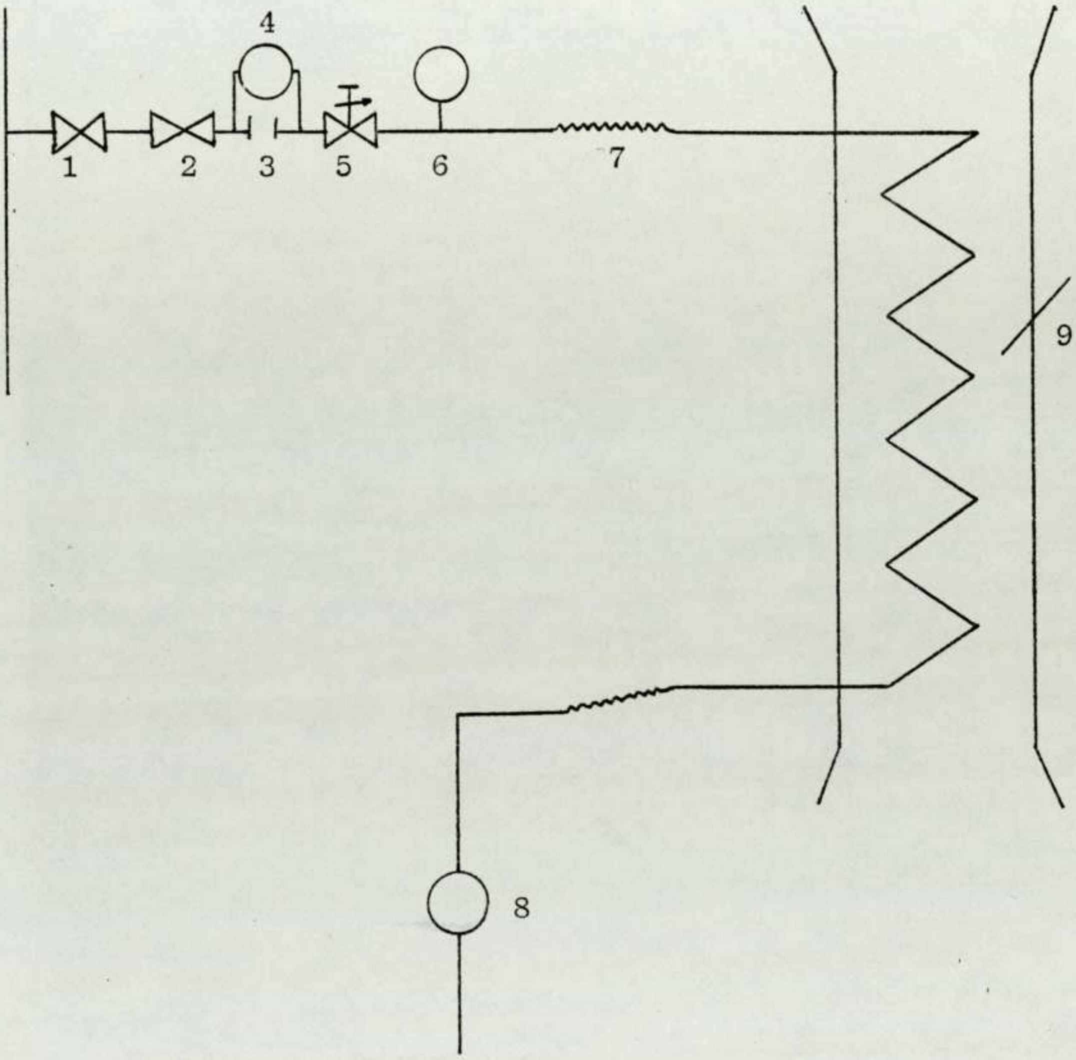


Figure A4.1 Reactor - Top and Side View



Legend:

1. Diaphragm valve
2. Reducing valve
3. Orifice plate
4. Pressure Sensor
5. Control valve
6. Pressure gauge
7. Flexible steam hose
8. Trap/strainer
9. Thermocouple

Figure A4.2 Reboiler Arrangement

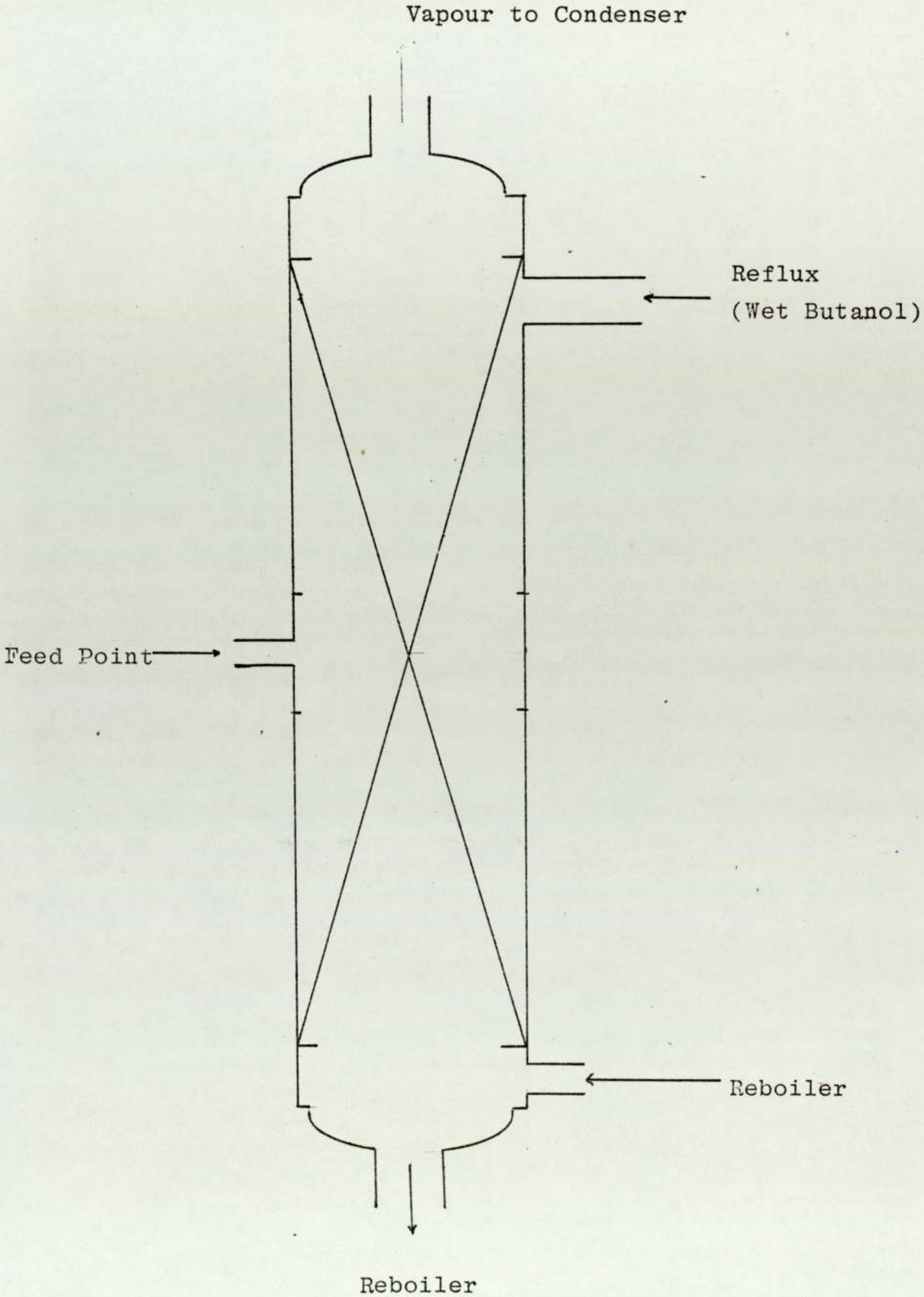


Figure A.4.3 Distillation Column

| | |
|---|---|
| Material | Q.V.F. |
| Length (m) | 2.5 |
| Diameter (cm) | 10 |
| Packing | Raschig Rings |

Table A.4.1 Distillation Column Specification

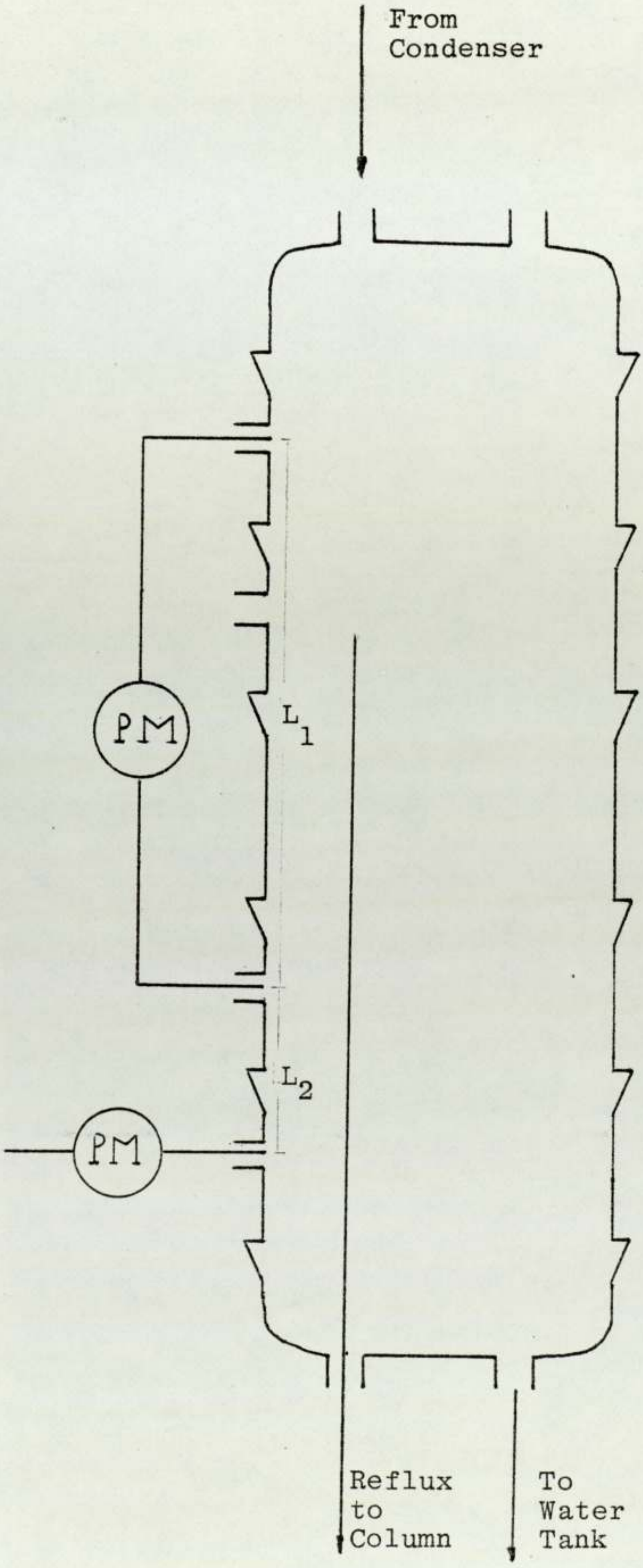


Figure A4.4 Decanter

| | |
|---|---|
| Material | QVF |
| Capacity (l) | 140 |
| Height (cm) | 172 |
| $L_1$ (cm) | 80 |
| $L_2$ (cm) | 80 |

Table A.4.2 Specification of the Separator

| | |
|---|---|
| Material | QVF |
| Surface area ($m^2$) | 1.2 |
| Steam Pressure (atm) | 1.0 |
| | 3.5 |
| Water evaporated (kg/h) | 14 |
| | 45 |
| Average Heat Transfer (Kcal/hm$^{2o}$C) | |
| Coefficient at 3.5 | 350 |
| Atmospheres (gauge) | |
| Free cross sectional area ($cm^2$) | 193 |
| Equivalent pipe diameter (cm) | 15.7 |
| Weight empty (kg) | 15 |
| Jacket capacity (litres) | 21 |
| Coil Capacity (lites) | 4.5 |
| Height (cm) | 71 |
| Diameter (cm) | 22.5 |

Table A.4.3 Specification of the Reboiler

| | |
|---|---|
| Material | QVF |
| Surface area ($m^2$) | 2.5 |
| Coolant throughput (kg/h) | 3100 |
| Steam condensed (mg/h) | 82 |
| Heat Transfer | |
| Coefficient (Kcal/$m^{2o}C$) | |
| (Jacket side-vapour to be condensed) | 250 |
| Coil side - cooling water | |
| Jacket side - liquid | 150 |
| Coil side - cooling water | |
| Free cross sectional area ($cm^2$) | 132 |
| Equivalent pipe diameter (cm) | 13 |
| Weight empty (Kg) | 14 |
| Weight full (kg) | 21 |
| Jacket capacity (litres) | 24 |
| Maximum coolant throughput (mg/h) | 3600 |
| Height (cm) | 79 |

Table A 4.4 Specification of the Condenser

| | Butanol | Formaldehyde | Xylol | Water |
|---|---|---|---|---|
| Material | stainless steel | stainless steel | QVF | QVF |
| Height (m) | 1.2 | 1.2 | - | - |
| Capacity (litres) | 1 36 | 1 36 | 20 | 50 |
| Shape | cylinder | cylinder | spherical | spherical |

Table A.4.5 Tanks Specification

# APPENDIX FIVE

# CALIBRATION OF THE THERMOCOUPLES

## The Calibration of Thermocouples

A computer program was written, that scans the five channels corresponding to the temperature measurements and prints to the corresponding readings, for the calibration of the thermocouples. Two temperatures were selected by obvious reasons. First, melting ice was used, giving consistently nil readings for the five channels. For the second measurement, boiling water was used. A thermometer indicated a temperature of 100°C.

Since all the readings at 0°C were nil, a linear relationship between voltage and temperature of the form

$$T(I) = b_i \times B(I) \qquad (1)$$

was assumed.

Where B(I) is the computer reading for channel 1, and T(I) the temperature corresponding to channel 1. Equation (1) can be written in the explicit form

$$T(I) = a_i \times \frac{B(I)}{1023} \times 5 \qquad (2)$$

since 5 volts corresponds to a reading of 1023 Table A.5.1 shows the results obtained.

| Location | Condenser | Top Column | Cool. Water | Reactor | Reboiler |
|---|---|---|---|---|---|
| Channel No. | 12 | 11 | 13 | 14 | 15 |
| Variable | B(11) | B(10) | B(12) | B(13) | B(14) |
|  | 845.1 | 838.4 | 826 | 828.1 | 832.9 |
|  | 845 | 838.1 | 826.1 | 827 | 833.5 |
|  | 846 | 838.1 | 826.3 | 828.4 | 832.5 |
|  | 846 | 838 | 825.6 | 828.4 | 833.6 |
|  | 845 | 838 | 825.8 | 828 | 833.6 |
|  | 845.2 | 838 | 825.7 | 828.2 | 833.2 |
| Max DesV% | 0.1 | 0.04 | 0.07 | 0.14 | 0.11 |
| Average Value | 845.4 | 838.1 | 825.9 | 828 | 833.2 |

Table A.5.1 Calibration of Thermocouples.

Using equation (2) the values of $a_i$ can be calculated,

$a_{10} = 24.41$ $a_{11} = 24.20$ $a_{12} = 24.77$ $a_{13} = 24.71$ $a_{14} = 24.56$

# APPENDIX SIX

## LOG-SHEETS OF EXPERIMENTAL RUNS

| Time | Resin Temp | Head Temp | Reboiler Temp | Cooling Water Temp | Condenser Temp. | Observations |
|---|---|---|---|---|---|---|
| 10.00 | | | | | | Formalin charged pH 4.2 +26 ml 1N NaOH |
| 10.11 | | | | | | N-butanol charged. Air to bottom valve. |
| 10.16 | | | | | | Steam on |
| 10.20 | | | | | | Melamine charged |
| 10.40 | 45 | | | | | Steam on to reboiler. |
| 10.50 | 81.4 | 82.5 | | 12.9 | 15.0 | Distilling (Air to bottom valve). |
| 11.05 | 93.8 | 89.5 | | 17 | 15.2 | Xylol charged. Steam to reactor down. |
| 11.20 | 95.1 | 88.2 | | 15.8 | 16.9 | |
| 12.00 | 97.4 | 87.3 | | 16.3 | 21.8 | 12 l aqueous phase removed |
| 13.00 | 98.1 | 86.4 | | 15.3 | 21.6 | 19 l |
| 13.30 | 99 | 85.9 | | 15.2 | 22.2 | 24 l |
| 14.00 | 99.8 | 85.5 | | 15.4 | 21.2 | 26 l |
| 14.30 | 100.7 | 85.8 | | 14.9 | 21.3 | 30 l aqueous phase removed acid catalyst added. |
| 15.00 | 101.2 | 88.9 | | 14.2 | 17.3 | 32 l |
| 15.30 | 103.5 | 86.8 | | 13.5 | 15.7 | 35 l Sample 1 |
| 16.00 | 107.6 | 86.4 | | 12.3 | 15.3 | white spirit tol. < 0.1 ml<br>37 l |

<u>Run 2</u>

continued/over

Table A.6.1- Run 2 - Log Sheet

Run 2

Table A.6.1- Run 2 - Log Sheet (Continued)

| Time | Resin Temp | Head Temp | Reboiler Temp | Cooling Water Temp | Condenser Temp | Observations |
|---|---|---|---|---|---|---|
| 16.30 | 111.3 | 90.5 | | 11.0 | 15 | 39 l |
| | | | | | | Heat off |
| | | | | | | Plant shut down |
| | | | | | | Resin sampled - Sample 2 |
| | | | | | | W.S.T. = 8 ml. |
| | | | | | | Viscosity = 4 PRS |
| 9.32 | 25.4 | | | | | Day after - Steam on |
| 10.20 | 96.7 | 82.7 | | 10.7 | 12.4 | Distilling |
| 10.50 | 107.9 | 95.8 | | 11.1 | 12.7 | 39.5 l aqueous phase |
| 11.00 | 109.6 | 89.7 | | 11.0 | 13 | W.S.T. = 11.3 ml Visc.= 7 PRS |
| 11.45 | 114 | 66.7 | | 9.4 | 13.5 | Addition of 8 l of butanol |
| 11.45 | 114.8 | 107 | | 9.0 | 13.5 | Reactor steam down |
| 12.30 | 115.4 | 87 | | 9.0 | 13.5 | 40.5 l aqueous phase |
| | | | | | | W.S.T. = 56.6 ml. |
| | | | | | | Visc. 4A-5 PRS |
| 12.50 | 116 | 88.7 | | 9.0 | 13.4 | Steam off 4.1 aqueous phase |
| | | | | | | W.S.T. = 50 ml. |
| | | | | | | Visc. 4A PRS |
| 15.00 | 60 | | | | | Discharge. |

| Time | T($^{o}$C) Reactor | T($^{o}$C) Head | T($^{o}$C) Reboiler | Dist. (1) | Observations |
|---|---|---|---|---|---|
| 9.00 | | | | | Formalin charged. |
| 9.15 | | | | | 50 cm$^3$ NaOH .pH = 6.1 |
| 9.30 | | | | | Butanol charged, Steam on |
| 9.37 | 40 | | | | Melamine charged (Compressed air on). |
| 9.50 | 81 | | | | Air off. Distilling. |
| 10.05 | 97.2 | 90.2 | 112 | | |
| 10.20 | 97.6 | 88.7 | 111.2 | | Xylol charged. |
| 10.50 | 96.6 | 88.3 | 111.9 | | |
| 11.20 | 97.6 | 87.4 | 119.8 | ~10 | |
| 11.50 | 99.3 | 87.8 | 122.7 | 14 | |
| 12.20 | 99 | 87 | 113.1 | 18 | |
| 12.50 | 99 | 86.9 | 115 | 22 | |
| 13.05 | 100 | 86.5 | 116.3 | 24 | Butanol (2) charged. |
| 13.20 | 101.5 | 35.4 | 109.3 | 27 | |
| 13.45 | 102.9 | 85.3 | 116.4 | 30 | Acid catalyst added. |
| 14.20 | 106.8 | 85.3 | 118 | 32 | |
| 14.50 | 110.7 | 92.3 | 122.6 | 36 | |
| 15.20 | 115 | 97 | 120.1 | 37 | WST = 11.5 ml Visc.= 3PRS |
| 15.50 | 117.9 | 69.4 | 110.7 | 38 | Low head temp. due to low boil up rate from reboiler. |
| 16.20 | 120 | 101.3 | 119.4 | 39 | Head temp high. Boil up rate reduced. WST = 17.8 Visc.= 4 PRS |
| 16.50 | 121.2 | 100 | 116.2 | 39 | |
| 17.20 | 120.9 | 100.4 | 116.9 | 39 | WST = 23.5 ml Visc. = 3A PRS |
| 18.20 | 120.6 | 97.6 | 116 | 39½ | Heat off. WST = 30.2 ml. Visc. = 3A PRS. |

Table A.6.2- Run 3 - Log Sheet

| Time | T($^{o}$C) Reactor | T($^{o}$C) Head | T($^{o}$C) Reboiler | Aqueous Phase | Observations |
|---|---|---|---|---|---|
| 9.15 | | | | | Charging Formalin |
| 9.20 | | | | | pH adjustment + 37ml NaOH pH=6.0 |
| 9.35 | | | | | Butanol charged. Steam on. |
| 9.50 | | | | | Melamine charged. |
| 10.05 | 95.1 | 89.3 | 117 | | Distilling. |
| 10.20 | 95.2 | 89.3 | 115.4 | | Xylol charged. Computer control |
| 11.20 | 96.7 | 88.4 | 100 | 10 | Reactor steam 20 psi |
| | | | | | Reboiler level low. |
| 12.20 | 97 | 88.3 | 106.8 | 18 | Reactor steam 18 psi |
| 13.05 | 98.1 | 87 | 109.8 | 25 | Butanol (2) charged. Reactor |
| | | | | | steam 24 psi. |
| 13.25 | | | | 30 | Black out. Steam off. |
| 14.05 | 97 | | | 30 | Computer restarted. Steam on. |
| | | | | | Acid Catalyst added. Reactor |
| | | | | | steam 24 psi. |
| 14.20 | 99 | 87.9 | 117 | 31 | |
| 15.20 | 109 | 90.8 | 114 | 37 | Sample (1) WST = 9.2 ml. |
| | | | | | Visc. = 4 PRS. Reactor steam 33 psi |
| 16.20 | 116.5 | 92.7 | 115.8 | 39 | Sample (2) WST = 12.5 ml |
| | | | | | Visc. = 8 PRS. Reactor steam 35 psi |
| 17.00 | | | | | 7. kg. Butanol added. |
| 17.20 | 117 | 104.6 | 116.4 | 39½ | Sample (3) WST = 21.5 Visc.=3A |
| | | | | | Reactor steam 34 psi. |
| 18.20 | 117.4 | 104.1 | 117 | 39½ | Sample (4) WST = 27.5 Visc.=4A |
| | | | | | Reactor steam = 34 psi. |
| 18.35 | | | | | Shut Down. Final sample. WST = 33 ml. |
| | | | | | Visc. = 5 PRS |

Table A.6.3 - Run 4 - Log Sheet

| Time | T($^{o}$C) Reactor | T($^{o}$C) Head | Aqueous Phase(1) | T($^{o}$C) Reboiler | Observations. |
|---|---|---|---|---|---|
| 9.30 | | | | | Formalin charged + 208 ml.<br>N NaOH pH = 5.8 |
| 9.34 | | | | | n-Butanol charged. Steam on. |
| 9.55 | 64 | | | | Melamine charged. |
| 10.00 | 96 | 88 | | 115 | Distilling. |
| 10.20 | 94.8 | 87.9 | | 115 | Xylol charged. |
| 11.20 | 95.3 | 87.7 | 10 | 111 | Steam line to reactor - 15 psi<br>Steam line to reboiler - 20 psi |
| 12.00 | 96 | 87.3 | 18 | 113.3 | Steam to reactor - 15 psi.<br>Steam to reboiler - 25 psi |
| 12.20 | 96.5 | 87.4 | 21 | 115.7 | Valve position. Reactor - 118<br>Reboiler - 130 |
| 13.00 | 96.4 | 87.9 | 25 | 110.6 | Butanol 2 charged. |
| 13.20 | 97.3 | 88.3 | 28 | 114.4 | |
| 14.00 | 100.4 | 87.8 | 31 | 115.4 | Acid catalyst addition. Steam line to reactor - 30 psi.<br>Valve position - 160 |
| 14.30 | 104.3 | 88.8 | 34 | 117 | |
| 15.05 | 112.4 | 93.7 | 37 | 113 | |
| 15.20 | 114.8 | 98.9 | 38 | 116 | Sample 1 WST = 10.5 ml.<br>Visc = 3A PRS |
| 16.20 | 120.4 | 102.5 | 39.5 | 117 | Sample 2 WST = 15.5 ml.<br>Visc = 3A PRS<br>Addition of 50 cm$^3$ of acid |
| 17.20 | 121.8 | 103.5 | 39.5 | 111 | Sample 3 WST = 22 ml.<br>Visc.= 3A PRS |
| 18.10 | 122.8 | 104.4 | 39.5 | 117 | Sample 4 WST = 29 ml.<br>Visc = 4A PRS |

Table A.6.4 - Run 5 - Log Sheet

| Time | T($^{o}$C) Reactor | T($^{o}$C) Head | T($^{o}$C) Reboiler | T($^{o}$C) Cooling Water | Observations |
|---|---|---|---|---|---|
| 10.45 | | | | | Melamine charged. |
| 10.50 | | | | | Distilling |
| 11.00 | | | | | Xylol addition. Computer Control.. |
| 12.00 | | | | | 10 ml of aqueous phase |
| 12.30 | | | | | 16 l steam line to reactor-15psi |
| 13.00 | 95 | 87 | 115.2 | 22.2 | 19 l of aqueous distillate |
| 13.30 | 95.3 | 37.3 | 114.8 | 20.7 | Addition of butanol (2) |
| 14.00 | 96.8 | 88.3 | 117 | 16.7 | 27 l of aqueous distillate. |
| 14.08 | 97.6 | 86.9 | 116 | 22.3 | 28 l of aqueous distillate. |
| | | | | | Acid addition. Reactor valve position = 160 |
| 14.45 | | | | | Boil up rate very low. Increase feed from reactor. Reactor valve position = 200 |
| 15.10 | 103 | 87.8 | 108 | 27.3 | 34 l of aqueous distillate. |
| 15.35 | 109.6 | 90.9 | 111 | 27.7 | 36 l of aqueous distillate. |
| 15.45 | | | | | Sample 1 Visc = 2 PRS WST = 2.5ml |
| 16.00 | 110..3 | 105.4 | 111 | 23.9 | 38 l of aqueous distillate. |
| | | | | | Steam to reactor increased. |
| | | | | | Valve position VP = 250 |
| 16.30 | 110.9 | 106 | 112 | 23.4 | 39 l of aqueous distillate |
| | | | | | Sample 2. |
| | | | | | Viscosity = 4A PRS WST = 11 ml. |
| 17.25 | 112.4 | 99.6 | 112 | 22.2 | Addition of 1 gal. butanol |
| 17.45 | 112.9 | 103 | 112.5 | | 40 l of aqueous distillate. |
| | | | | | Viscosity = WST 19.7 $cm^3$ |
| 18.20 | 113.7 | 102 | 113 | 22 | |
| 18.45 | 113.6 | 102 | 113 | 22 | Sample 4. Viscosity = 3A PRS<br>WST = 33 ml. |

TableA.6.5 - Run 6 - Log Sheet

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