CHEMICAL KINETIC INVESTIGATION OF A COMMERCIAL BATCH REACTOR PROCESS

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SUMMARY

The aim of this investigation was to study the chemical reactions occurring during the batchwise production of a butylated melamine-formaldehyde resin, in order to optimise the efficiency and economics of the batch processes. The batch process models are largely empirical in nature as the reaction mechanism is unknown.

The process chemistry and the commercial manufacturing method are described. A small scale system was established in glass and the ability to produce laboratory resins with the required quality was demonstrated, simulating the full scale plant. During further experiments the chemical reactions of methylolation, condensation and butylation were studied. The important process stages were identified and studied separately. The effects of variation of certain process parameters on the chemical reactions were also studied.

A published model of methylolation was modified and used to simulate the methylolation stage. A major result of this project was the development of an indirect method for studying the condensation and butylation reactions occurring during the dehydration and acid reaction stages, as direct quantitative methods were not available. A mass balance method was devised for this purpose and used to collect experimental data. The reaction scheme was verified using this data. The reactions stages were simulated using an empirical model. This has revealed new information regarding the mechanism and kinetics of the reactions. Laboratory results were shown to be comparable with plant scale results.

This work has improved the understanding of the batch process, which can be used to improve product consistency. Future work has been identified and recommended to produce an optimum process and plant design to reduce the batch time.

Key Words:

Butylated melamine-formaldehyde resin, Coating Resin, Chemical Kinetics, Batch Reactor Process, Process Modelling and Simulation.

DEDICATED TO

SHRI KRISHNA

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CHAPTER ONE

INTRODUCTION

The work presented in this thesis is the outcome of a research project which was divided into two phases. Firstly, part of the project work was carried out as a Research Associate for the Teaching Company set up between BIP Chemicals Ltd and the University of Aston in Birmingham. The second phase, after the end of the Associateship, was carried on further as a research student in the Department of Chemical Engineering at Aston University.

The BIP/Aston University Teaching Company Scheme (TCS) was commenced in May 1983. The overall aim of the scheme was to optimise the efficiency and economics of the batch processes used for synthetic resin manufacture, to give the Company financial savings, and a product with more closely controlled properties.

The production process for a butylated melamine-formaldehyde resin was investigated and the required actions were recommended to produce a consistency in process operations and product quality. The project was split into several areas of work. These included recovered solvent analysis, solvent recovery plant operations, control parameter identifaction, development of a process model and design of a computer-aided control scheme. There were four associates involved in the scheme, working in separate areas of the project. The scheme was very successful as most of the objectives were achieved. A computer-aided batch control strategy, applicable to all types of coating resin was developed. A microcomputer was interfaced to one of the plant batch reactors and used to demonstrate the feasibility of computer control using new control parameters. A model was developed for the various stages of the batch process. This has improved the understanding of the process and confirmed the proposed control parameters. A process control scheme based on the model was not implemented, because of difficulties with the on-line measurement of the chemical species involved.

During the course of the TCS project, the work was reported quarterly in the form of a written report and a presentation to the Management Committee, which included senior managers from BIP, lecturers from the University and a representative from Science and Engineering Research Council (SERC). The work was critically examined by the members of the Management Committee and also by the scientists in the Research Department of BIP Chemicals Ltd. The scheme finished in March 1986. Two other members of the scheme have submitted theses [1,2] covering different areas of the work. This thesis is concerned with the offline analysis and process modelling.

The type of resin under investigation for the batch production, was butylated melamine-formaldehyde (butylated M-F) resin, more commonly known as a coating resin as it is widely used in the coating industry as a cross-linking agent. In general, it comes under the term etherified amino-formaldehyde resin. This term covers three basic categories of coating resins, as either melamine, urea or benzoguamine can be used in the resin formulation to provide the basic amino groups which are required in the complex reactions which take place. Either normal-butanol or iso-butanol can be used for the etherification with an associated impact on the resin produced. The process plant was used to produce a wide range of different products, using a batch process.

The butylated M-F resins are the oligomers (polymers with low molecular weights) of methylol melamine properly etherified with either normal or iso butanol. Etherification of the methylol group is necessary to make the resin-product compatible with solvents and other film-forming polymers or oligomers and to give sufficient storage stability.

BIP has been manufacturing butylated M-F resins for approximately forty years. The batch process models are, however, largely empirical in nature as the reaction mechanism is unknown. The reactors are largely manually operated, as a result of which product quality can be variable and from time to time batches of product fall outside the specification limits. This necessitates expensive rework procedures or the costly loss of a complete batch. The chemistry involved in the resin-making process is very complex. The relevant literature is very limited . In addition to this, the qualitative measurement of some of the chemical groups involved is not possible directly.

The perfomance characteristics of a butylated M-F resin during its end use (cross linking process), depend upon its structure and the distribution of various functional groups. The three main factors which are responsible for the structure and the functional groups are (a) the molar amounts of formaldehyde combined, (b) the molar amounts of butanol combined and (c) the molecular weight distribution. These three factors can vary from batch to batch and hence they are responsible for some variations in the product quality.

Therefore, the objectives of this research work were as follows:

(1) To devise an indirect method for the analysis of the chemical groups involved and hence to investigate the chemistry involved in the process.
(2) To improve the understanding of the reactions taking place throughout the stages of the batch process.
(3) To develop a model for the batch production of butylated M-F resins.

Laboratory experiments were carried out to gain an understanding of the production process and associated problems. Confidence was developed that these experiments produced resin product with a given specification. The manufacturing process was considered in six well defined stages. The three stages which involve chemical reactions were studied in detail with a veiw to producing a process model. These stages are known as Methylolation, Dehydration and Acid Reaction.

An indirect method was devised to study the chemical changes occurring during the process. The method uses various analytical techniques and mass balances to produce data regarding the changes in quantities of some chemical groups. The method was applied to a series of laboratory and plant scale experiments. Experiments were also carried out to study the effect of variations in some process parameters such as pH and butanol concentration. It was concluded from the work that the analysis is adequate and reliable for collecting experimental data.

A reaction scheme has been postulated and validated by using the stoichiometry of the postulated scheme to interpret the experimental results. This work has revealed new facts regarding the mechanism and kinetics of the chemical reactions involved.

A model has been developed for the various stages of the resin-making process, which gives an improved process knowledge. This has identified some process parameters which can be used for a better control of the process to produce products with more closely controlled properties.

The three main reactions which occur during the process are, methylolation, condensation and butylation. At BIP, the condensation reaction was considered to be occurring in two ways, producing methylene bridges and methylene ether bridges. However, this work has proved that the condensation reaction occurs in only one way producing methylene ether bridges and not methylene bridges.

It was believed at BIP that condensation is the main reaction during the dehydration stage and butylation is the main reaction during the acid reaction stage. The acid reaction stage was generally known as an etherification stage. However, this work has proved that both reactions occur simultaneously during these stages and it is necessary to control the relative proportions of these reactions to produce the desired product. In fact, more than 60% of the total butylation occurs during the dehydration stage.

The batch time for the resin production varies from 12 hours to 19 hours, depending upon different reactor efficiencies. This work has shown that only four to five hours are involved in the chemical reactions. The chemical changes occurring during the remaining periods are very small. These periods are mainly involved in removing water from the reactor system.

CHAPTER TWO

PROCESS CHEMISTRY

2.1 INTRODUCTION

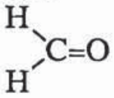
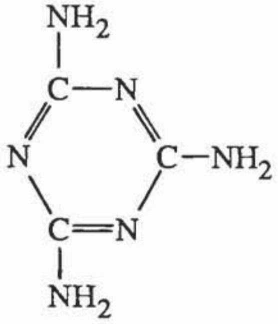
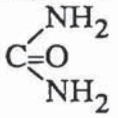
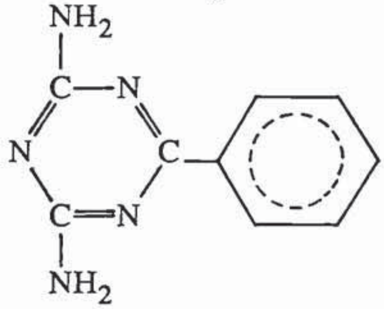
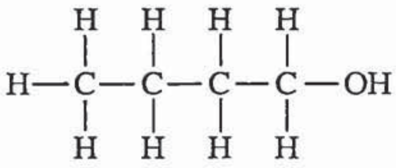
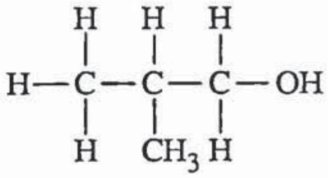
The basic chemistry of butylated melamine-formaldehyde resin formation is very complex as there are three chemical reactions involved in the process and two of them occur simultaneously. The reaction path depends on parameters such as pH, concentration, molar ratio, temperature, reaction time and on the sequence of reactions which permit large number of permutations and result in a complex system. The chemistry was poorly understood because of this complexity and also because of the difficulties encountered in the qualitative and quantitative measurement. Improved analytical techniques, including nuclear magnetic resonance method, are now available.

This chapter starts with some information on the raw materials necessary for the production of butylated amino formaldehyde resins. The experimental work was carried out using a commercial resin hereafter known as Type A resin, which is a melamine-formaldehyde resin butylated with n-butanol. The basic chemistry of the process is described in this chapter for this particular resin, including a critical review of the available literature. The detail of the experimental and modelling work is given in chapters 4 to 7. The results have been used in this chapter, whenever this adds to understanding of the process chemistry.

2.2 RAW MATERIALS

The three reactants in the production of butylated amino formaldehyde resins are (a) formaldehyde, (b) melamine, urea or benzoguamine and (c) iso-butanol or normal-butanol. Chemical structures of these reactants are shown in Table 2.1.

Table 2.1 Reactants used in the production of butylated coating resins

Compound	IUPAC Name and Chemical Structure	Mol. Wt.
Formaldehyde	Methanal 	30.03
Melamine	2, 4, 6-Triamino-s-Triazine 	126.10
Urea	Carbonyl - diamide 	60.06
Benzoguamine	2, 4-Diamino-6-Phenyl-s-Triazine 	187.20
Normal-Butanol	1-Butanol 	74.12
Iso-Butanol	2-methyl-1-propanol 	74.12

2.2.1 Formaldehyde

The chemistry of formaldehyde and its compounds has been well described by Meyer [3]. Pure monomeric formaldehyde, 'CH_2O', is a colourless pungent gas with a boiling point of -19 °C. It converts into a mixture of several different derivatives. The most common compounds listed in Table 2.2 have been described by Meyer [3] giving some data on each of them. For more detail, Meyer has recommended the comprehensive and excellent reviews of Walker [4] and Imoto [5]. In pure form formaldehyde polymerizes; in aqueous or alcoholic solutions it undergoes polymerization as well as solvolysis, reactions with the solvent.

Table 2.2 Species in Commercial Formaldehyde [3]

Commercially the following forms are available: Formalin, Aqueous solution containing a variety of concentrations of formaldehyde and methanol, Paraformaldehyde, in powder or flake form called Paraform, and formaldehyde solutions in alcohols called Formals.

Paraformaldehyde is a mixture of polyoxymethylene glycols, $H(CH_2O)_nOH$ with n ranging from 6 to 100. It forms in the following way: Solid and liquid monomeric formaldehyde is unstable and at -90 °C both spontaneously polymerize, forming solid polymeric oxymethylene chains $-(CH_2O)_n-$. These are hygroscopic and form polyoxymethylene glycol. The reaction is reversible. It is commercially available as powder (95% wt) and as flake (91% wt).

Formalin is an aqueous solution usually containing 35 to 44 wt% formaldehyde and 3 to 10 wt% methanol. The solubility of formaldehyde depends on temperature and purity. In a pure aqueous solution formaldehyde is less soluble than in presence of methanol. Thus methanol is used as a stabilizer. Formaldehyde is present largely as an equilibrium mixture of methylene glycol and polyoxymethylene glycols in aqueous solution. The equilibrium in aqueous solution can be represented by the following reaction scheme:

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2$$ Methylene glycol

$$2\,CH_2(OH)_2 \rightleftharpoons HO(CH_2O)_2H + H_2O$$ Dioxymethylene glycol

$$HO(CH_2O)_2H + n\,CH_2(OH)_2 \rightleftharpoons HO(CH_2O)_{n+2}H + n\,H_2O$$
Polyoxymethylene glycol

Aqueous solutions contain less than 0.1% of formaldehyde in monomeric form [3]. The concentration of the various polymers is not yet accurately known. It changes with total formaldehyde concentration, temperature and methanol concentration. The action of methanol is chemical, not physical. Methanol promotes subsequent depolymerization of polyoxymethylene glycol forming hemiacetals as follows:

$$HO(CH_2O)_nH + CH_3OH \rightleftharpoons HO(CH_2O)_{n-1}H + CH_3OCH_2OH$$
monomeric hemiacetal

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

Dankelman [6] has shown the formation of various hemiacetal quantitatively, with the help of proton NMR spectroscopy. These hemiacetals are soluble in water, and thus methanol increases the solubility of glycols.

During storage, formaldehyde solutions age due to polymerization and hence to prevent precipitation, they must be kept above the recommended storage temperature at all times. Formaldehyde gas is flammable and forms explosive mixtures with air and oxygen. At room temperature the explosive range is 7 - 73% by volume of formaldehyde per volume of air. When aqueous or alcoholic formaldehyde solutions are heated above their flash points a potential explosion hazard exists.

In this work, commercial formalin containing 44 Wt% solution of formaldehyde in water with about 3.5 Wt% methanol was used.

2.2.2 Melamine, Urea or Benzoguamine

These three reactants contain the amino groups ($-NH_2$) required in the complex reactions which take place during the manufacturing of amino resins. Therefore, either melamine, urea or benzoguamine is used in the resin formulation to give the three categories of coating resins. They are all solids under normal conditions and charged as powders to the process plant.

For the resin under investigation, Type A, melamine was used. It is a microcrystalline powder, free from impurities. Each melamine molecule contains three amino groups as shown in Table 2.1. Though melamine is the term most commonly used, it is also known in the literature as 2,4,6-triamino 1,3,5-triazine, as cyanuric acid amide, and as cyanuric triamide [7].

2.2.3 Normal-Butanol or Iso-Butanol

Either n-butanol or iso-butanol can be used with some effect on the properties of the resin produced. The scope of this work is limited to the use of n-butanol.

It is a clear colourless liquid with an unpleasant vinous type odour and the following physical properties:

Molecular Weight	74.12	
Boiling Point	117.5	°C
Flash Point	33	°C
Vapour Pressure	4.3	mm Hg at 20 °C

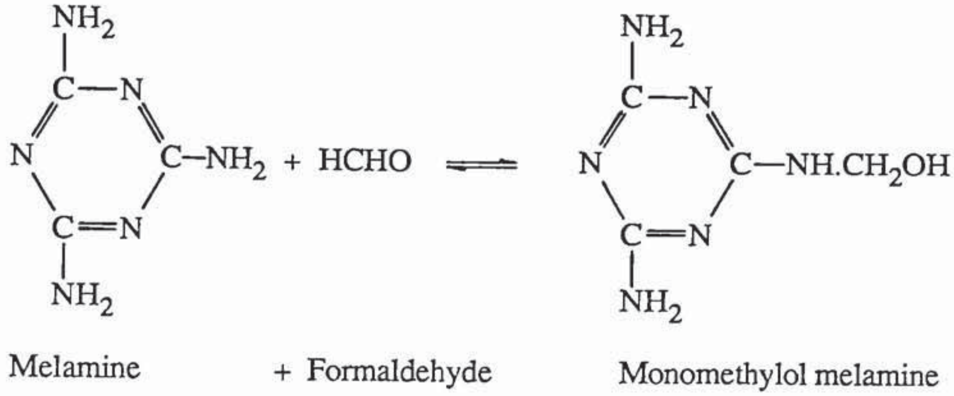
2.3 CHEMICAL REACTIONS

The chemical changes occurring during the production of Type 'A' resin have been studied in detail using various analytical techniques and mass balances. This is discussed in Chapters 4 to 7. The process is described in Chapters 3 and 4. Three reactions which occur during the process are methylolation, condensation and butylation. Each reaction is discussed separately in the following sub-sections.

2.3.1 Methylolation Reaction

Methylolation is an addition reaction in which formaldehyde combines with melamine to form methylol melamines. This reaction occurs first and forms functional groups called 'methylols' ($-CH_2OH$) which react further during the butylation and condensation reactions.

The melamine molecule contains three amine groups and hence has six reactive hydrogen atoms . Depending on the initial molar ratio and reaction conditions, the addition reaction between melamine and formaldehyde consists of the conversion of melamine into nine different methylol melamines ranging from mono to hexamethylol melamine [8-10]. There are two isomers of di, tri and tetramethylol melamines. The reaction scheme forming a monomethylol melamine is shown in equation 2.1. The two possible isomers of trimethylol melamine have been illustrated in Figure 2.1.



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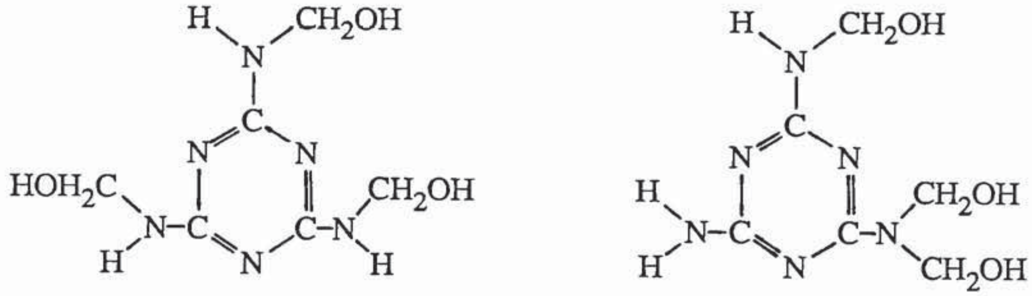
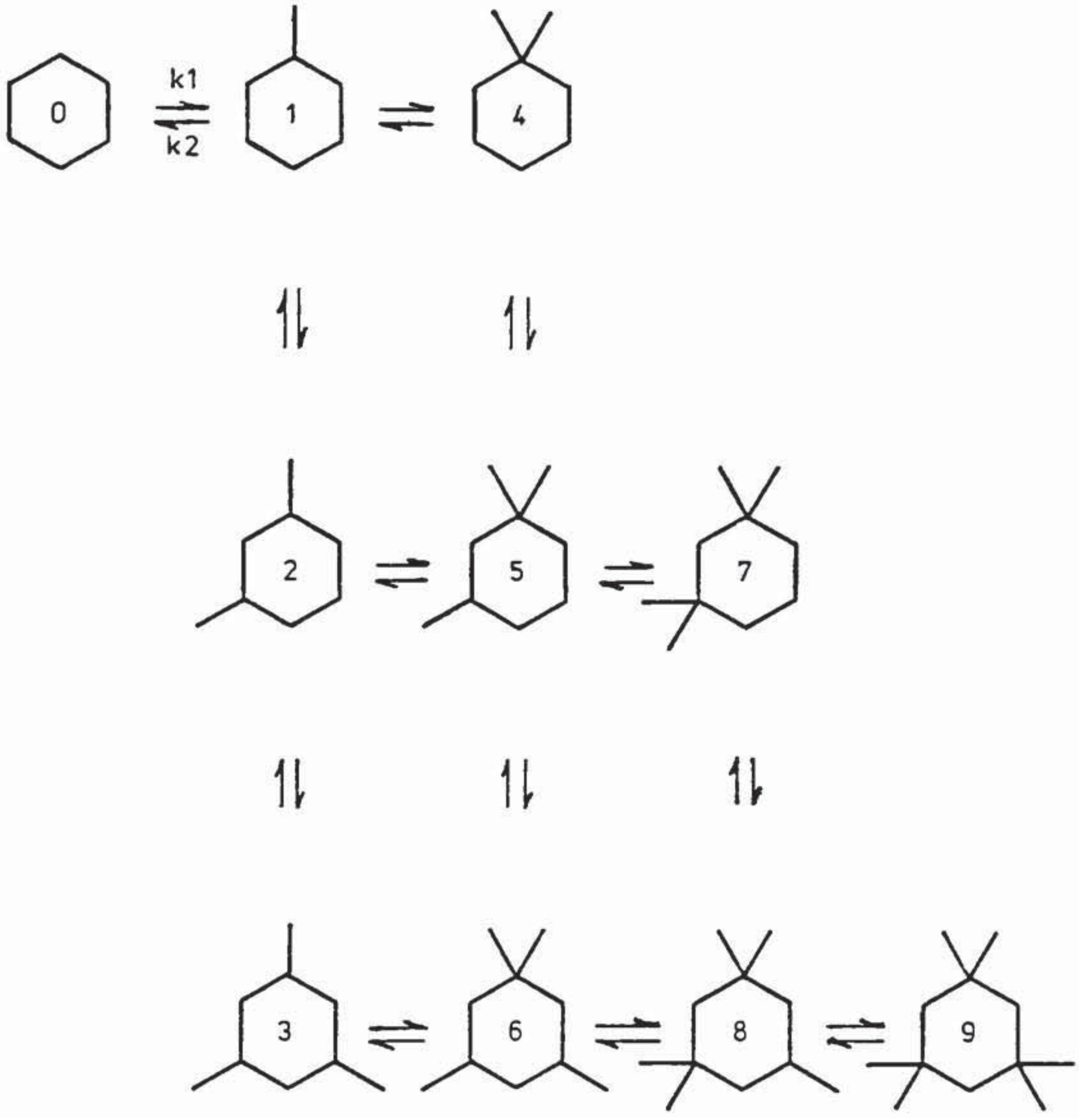


Figure 2.1 Isomers of trimethylol melamine

The schematic diagram used by Aldersley et al [9] to show all possible methylolation and demethylolation reactions starting with melamine and ending with the formation of hexamethylol melamine is given in Figure 2.2. In this case, the forward rate constant, k_1, was considered to be second order for all the methylolation (forward) reactions, whereas the backward rate constant, k_2, was considered to be first order for all the demethylolation (backward) reactions. All nine methylol melamines have been numbered from 1 to 9 in Figure 2.2 for further references.

For the process under investigation the addition reaction reaches equilibrium within forty minutes. The degree of addition was found to be around four. That means averagely four methylols ($-CH_2OH$) can be formed per melamine molecule. The simulation of the addition stage based on analysis for free formaldehyde concentration, also yielded the concentrations of all nine methylol melamines (See Chapter 7).



k_1 = Second order forward rate constant

k_2 = first order backward rate constant

Figure 2.2 Scheme of all possible methylolation and demethylolation reactions starting with melamine (top left) and ending with the formation of hexamethylol melamine (bottom right)

2.3.1.1 Literature on the Methylolation Reaction

This reaction was studied by several scientists [7, 12-15] in 1940's and 1950's. However, the useful information on the kinetics of the methylolation reaction has been published in the last twenty years.

In 1966 Gordon et al [8] studied the kinetics and equilibria of the addition reaction between melamine and formaldehyde. The reaction was kinetically separated from the subsequent condensation stage by suitable choice of concentration and temperature conditions. The reaction was monitored by estimation of the free formaldehyde content of the system. This was determined by using a modification of the iodine-sulphite method as used by De Jong and De Jonge [11]. The reaction was studied over a range of the mean degree of methylolation between 1 and 3.7, a temperature range 25 to 55 °C, and a pH range 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 kinetics of the reactions were described in terms of the random reaction scheme and a number of average kinetic and thermodynamic constants was calculated. While treating the results Gordon et al [8] realised that deviations do occur from randomness and they described the factors which are likely to cause this.

In 1968, Aldersley et al [9], including the same authors, re-investigated the kinetics and equilibria of this reaction in detail. Two structurally different substitution effects, a local effect confined to a single amino group and a general effect over the three amino groups of a given melamine nucleus, were introduced to account for the deviations from randomness. These can be described as follows. (a) The Local effect : If one hydrogen of a particular amino group has already reacted with formaldehyde, the reactivity of the second hydrogen will be less than that of the first one. (b) General effect : If r ($r = 1,2,...5$) hydrogen atoms of a melamine nucleus are methylolated then the reactivity of the $r+1$ hydrogen will be less than that of the previous one. They postulated the linear form of these effects as follows:

$$\Delta G_r = \Delta G^* + r\,\Delta G_g + \Delta G_l$$

Where r ΔG_g is the free energy contribution due to the general effect, in adding a methylol group to a melamine already bearing r methylols. ΔG_l is the free energy contribution due to the local effect. ΔG_r is the overall standard free energy change. ΔG^* is the quantity in absence of substitution effects. Figure 2.2 shows that ΔG_r is not unique, e.g. for r=2, trimethylol melamines can be formed from 2 to 5, 4 to 5 or 2 to 3.

For the random reaction $\Delta G_g = \Delta G_l = 0$. N_g and N_l are defined in terms of ΔG_g and ΔG_l:

$$N_g = \exp -(\Delta G_g / 2RT)$$

$$N_l = \exp -(\Delta G_l / RT)$$

For the random reaction $N_g = N_l = 1$.

Their non-random model consists of eleven differential equations for the rate of change in the concentrations of melamine, formaldehyde and nine methylol melamines with respect to reaction time. The model has been listed in Chapter 7.

The model included the substitution effects in the following way. The forward rate constant k_1, for adding a formaldehyde molecule to a melamine nucleus already bearing r methylols, is multiplied by N_g^r, and further multiplied by $N_l^{1/2}$ if the addition occurs at a secondary amino group. The constant of the corresponding back reaction k_2, will be multiplied respectively by N_g^{-r} and $N_l^{-1/2}$.

The reaction was followed by titration of the free formaldehyde as a function of time. The process conditions used to study the reaction are given below:

Temperature = 45 °C constant
pH = 9.5 constant
Formaldehyde / Melamine (F/M) molar ratio = 5

As a result of their equilibrium study and kinetic interpretation they determined the following rate constants and model parameters for the optimum fit to their experimental results.

Equilibrium constant $K = 0.2208$ mol / l
Second order forward rate constant $k_1 = 1.412$ l / mol. hr
First order backward rate constant $k_2 = 0.3118$ 1 / hr
General substitution effect $N_g = 1$
Local substitution effect $N_l = 0.61 \pm 0.03$

In fact they found $N_g = 1.011$ for the optimum fit, but afterwards they concluded that the general substitution effect is negligible and can be neglected i.e. $N_g = 1.0$.

Tomita [10] studied the addition reaction by the direct observation with NMR spectroscopy and high speed liquid chromatography. He used the liquid chromatographic technique for the quantitative analysis of methylol melamines in the reaction mixture. He determined the free formaldehyde content of the reactant mixtures by iodine-sulphite, ammonium chloride and potassium cyanate titration methods. He found these methods too troublesome and suggested the need of a more convenient method. The molar concentration of free formaldehyde at equilibrium state was determined using the liquid chromatographic technique.

Tomita presented a kinetic model using the same reaction scheme but instead of keeping the forward and backward rate constants same for all reversible reactions, he considered them separately for each reversible reaction and estimated the equilibrium constants and rate constants for the individual reversible reactions. He studied the addition reaction using seven different F/M molar ratios (F/M = 1, 3, 5, 7, 10, 15 and 30) at three constant temperatures (28, 38 and 48 °C) and at constant pH equal to 9.0. For each of these experiments he reported methylol distribution at equilibrium and equilibrium constants for all reversible reactions.

From the analysis of his experimental and kinetic results, Tomita concluded that the methylolation of melamine nuclei becomes more dofficult with successive additions. The forward rate constant for the last stage of additions to produce hexamethylol melamine, was found to be one tenth of that for the initial stage of additions to produce monomethylol melamine.

Tomita's experimental results also shows that just six methylols (1 to 6 shown in Figure 2.2) can be produced using the molar ratio F/M = 5, at 48 °C constant temperature, whereas all nine methylols can be produced using the higher molar ratios (F/M = 15 or 30) at the same constant temperature. Tomita did not find the presence of any condensation product in the experiment which was carried out at 80 °C.

In this work, the model reported by Aldersley et al [9] has been tested against the more precise and reliable experimental data published by Tomita [10] who measured seven more precise variables instead of one variable as a function of time. This will be discussed in detail in Chapter 7. New values of the model parameters, N_g and N_l were found as a result of this model fitting. The modified model was then used to simulate the addition stage of the process, allowing for changes in the process conditions. The values found for the model parameters are as follows:

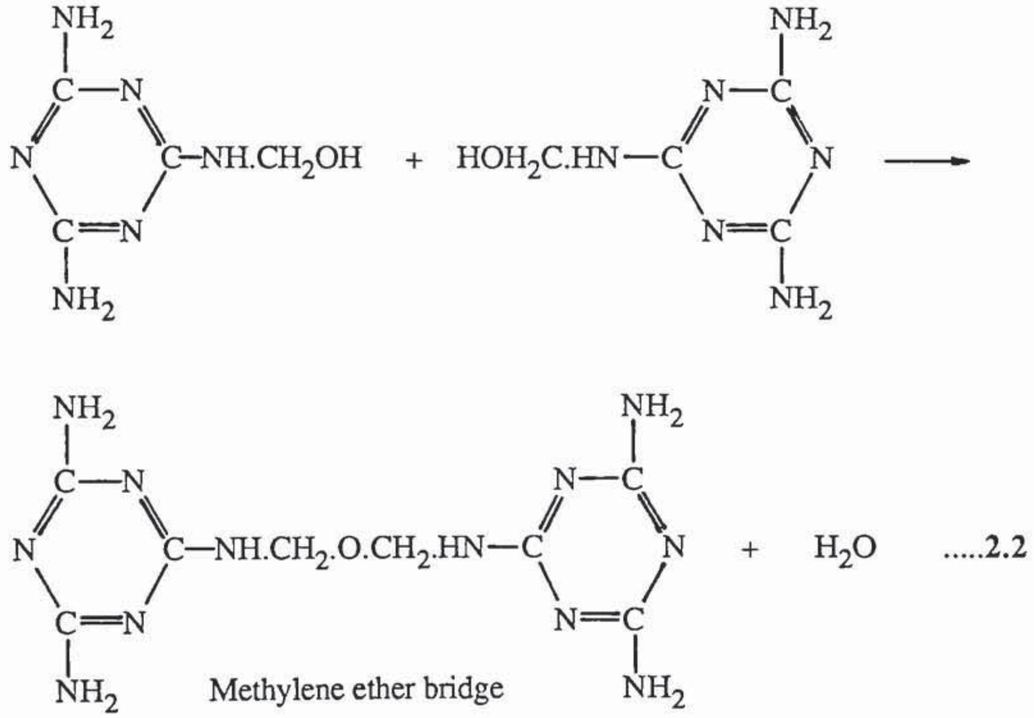
$N_g = 0.93$ and $N_l = 0.59$

Previously the general substitution effect was neglected by Aldersley et al [9] and the model parameter N_g was considered to be 1.0. However, during this work, the value of N_g was found to be 0.93. This result reveals the important fact that the general substitution effect is also present although it is a lesser effect than the local substitution effect, where the model parameter N_l is equal to 0.59.

2.3.2 Condensation Reaction

This is the polymerization reaction in which the methylol melamines, formed by the addition reaction, react together liberating water of reaction. For the process under investigation, this reaction occurs in the following way. Two methylol groups from two methylol melamine molecules react together to form a methylene ether bridge as in equation 2.2.

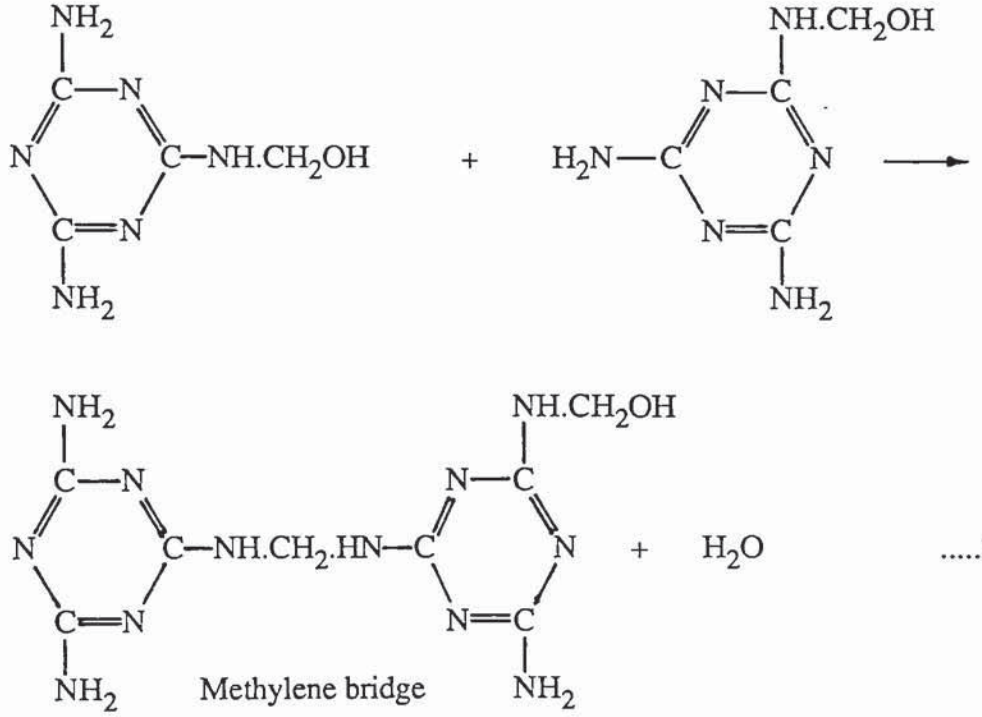
Methylene ether bridge formation



In the literature [7, 13, 16-20], another reaction has also been considered, in which a methylol group from one methylol melamine reacts with an amino group hydrogen from another to form a methylene bridge as in equation 2.3. The reaction conditions used in these cases were, however, not the same as those used in the process under investigation. This reaction has been excluded from the present scheme. This is discussed in section 2.4.2.2.

As the condensation reaction proceeds forming methylene ether bridges, the chain length increases and a viscous resin is produced. In this way, polymers with various chain length and hence molecular weights are formed. The greater the degree of polymerization, the more viscous the resin becomes. For the resin, Type A, under investigation the degree of polymerization was found to be about 4 (see Chapter 8).

Methylene bridge formation



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2.3.2.1. Literature on Condensation Reaction

Okano and Ogato [13] investigated the kinetics of the condensation of melamine with formaldehyde in aqueous solution at 35, 40 and 70 °C, with a pH range from 3 to 10.6. They employed both iodometric and sulphite methods to determine the rates of formation of methylol melamines and methylene bridges. They considered the formation of methylene bridges only by an irreversible condensation reaction. The condensation rate was expressed as second order in melamine concentration and first order in formaldehyde concentration. The following reaction mechanism was suggested:

$$MCH_2OH + H_3O^+ \rightleftharpoons M^+CH_2 + 2H_2O \quad (\text{fast})$$

$$M^+CH_2 + MH \longrightarrow MCH_2M + H^+$$

Where MH is a molecule of melamine. The methylene bridge formation reaction between melamine molecules was considered to proceed by way of a rate determining attack of the conjugate acid of methylol melamine on free melamine.

Wohnsiedler [16] found that the condensation reaction takes place mainly by the formation of methylene bridges. However, he considered the possible formation of methylene ether bridges in an alkaline medium. Hodgins et al [7] and Kitagawa [17] found the formation methylene bridges and methylene ether bridges during the condensation reaction. Kambanis and Vasishth [18] during the studies of UF resins, found that the condensation takes place through the formation of only methylene bridges in acidic conditions and only methylene ether bridges in alkaline conditions. Gams et al [21], as cited by Wohnsiedler [16], studied the condensation reaction and found mainly the formation of methylene ether bridges and assigned minor role to the methylene bridges as a polymer forming linkage.

Sato [19, 20] investigated the condensation reaction in acidic media and found mainly the formation of methylene bridges. The condensation mechanism was considered to be an attack of the electrophilic carbon of the amino-methylol group on the nitrogen of the amino or amino-methylol group of a methylol melamine. The condensate was found less basic than the starting methylol melamine. The condensation rate equation was written as a sum of three terms :

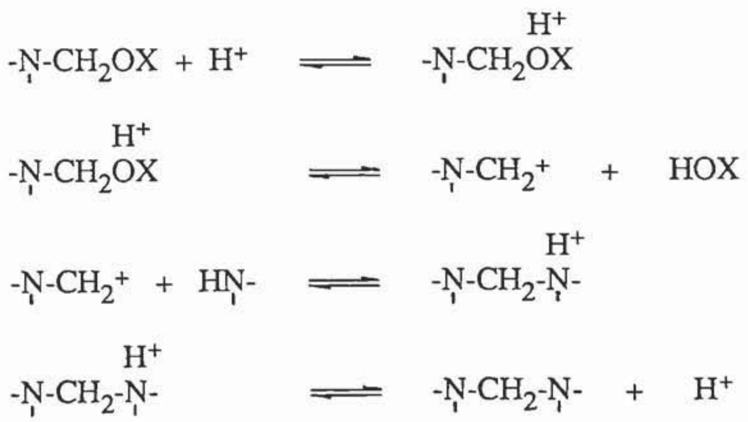
$$\begin{aligned} Rc = {} & k_1[MCH_2OH]^2 \quad (\text{ molecular form, molecular form }) \; + \\ & k_2[MCH_2OH]\,[HM^+CH_2OH] \quad (\text{ molecular form, conjugate acid }) \; + \\ & k_3[HM^+CH_2OH]^2 \quad (\text{ conjugate acid, conjugate acid }) \end{aligned}$$

where k_1, k_2 and k_3 are respective rate constants of the elementary reactions. The presence of the conjugate acid of a methylol melamine is dependent on the pH of the solution.

$$MCH_2OH + H_3O^+ \rightleftharpoons HM^+CH_2OH + H_2O$$

Dixon et al [12] investigated the dissociation constants of melamine and its compounds. They found that the hydrogen ion concentration is a factor in controlling the rate of polymerization and consequently the basicity of polymerizing melamine compound affects the acidity of its solution and therefore, in turn influences the rate of polymer formation.

Portugal [22] has described the following mechanism, given by Berge [23], for the condensation forming methylene bridges :



$$(1) \quad \text{-}\underset{|}{N}\text{-}CH_2OX + H^+ \rightleftharpoons \text{-}\underset{|}{N}\text{-}CH_2\overset{H^+}{O}X$$

$$(2) \quad \text{-}\underset{|}{N}\text{-}CH_2\overset{H^+}{O}X \rightleftharpoons \text{-}\underset{|}{N}\text{-}CH_2^+ \quad + \quad HOX$$

$$(3) \quad \text{-}\underset{|}{N}\text{-}CH_2^+ + H\underset{|}{N}\text{-} \rightleftharpoons \text{-}\underset{|}{N}\text{-}CH_2\text{-}\overset{H^+}{\underset{|}{N}}\text{-}$$

$$(4) \quad \text{-}\underset{|}{N}\text{-}CH_2\text{-}\overset{H^+}{\underset{|}{N}}\text{-} \rightleftharpoons \text{-}\underset{|}{N}\text{-}CH_2\text{-}\underset{|}{N}\text{-} \quad + \quad H^+$$

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.

In 1977 De Breet et al [24] applied ^{13}C-NMR (Nuclear Magnetic Resonance) spectroscopy to the analysis of resins containing formaldehyde. The work showed that ^{13}C-NMR spectroscopy is a powerful tool for the analysis of resins containing formaldehyde. They studied a methylated melamine fomaldehyde resin and the ^{13}C-NMR shifts of various functional groups measured are summerized in Table 2.3. Braun et al [25] showed that gas chromatography, infra red and H-NMR all confirm that contrary to the older literature methylene bridges are absent in condensation products formed under alkaline conditions. They considered the following reaction scheme:

$$\text{C-NH}_2 + \text{HCHO} \rightleftharpoons \geqslant\text{C-NHCH}_2\text{OH}$$

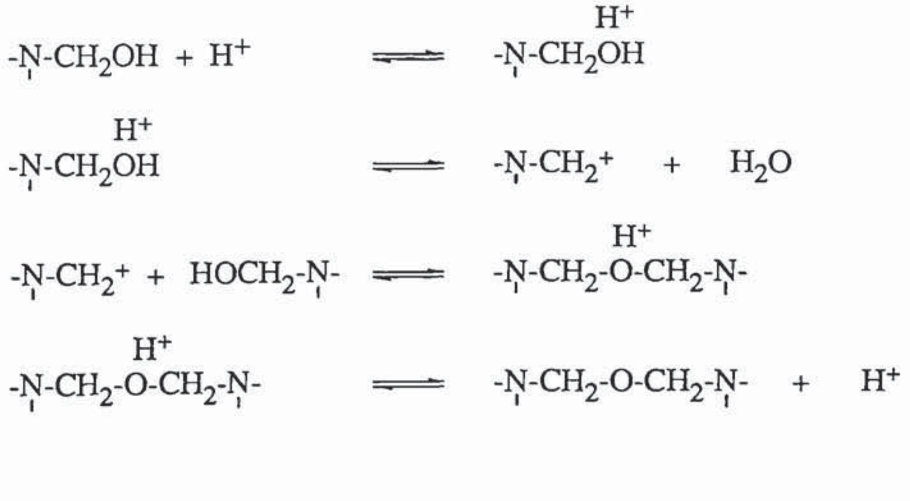
$$2\ \text{C-NHCH}_2\text{OH} \rightleftharpoons \geqslant\text{C-NHCH}_2\text{OCH}_2\text{NH-C}\leqslant + \text{H}_2\text{O}$$

Table 2.3 Chemical NMR shifts of Carbon atoms in melamine [24]

In 1978 Dawbarn et al [26] examined some melamine formaldehyde resins by ^{13}C-NMR spectroscopy. The resin preparation was carried out at pH 9 and 100 °C with a formaldehyde to melamine ratio of 6:1. Under these conditions, no methylene bridges were found. They concluded this because there were no resonances visible in the region 47-54 ppm where the carbon atoms within the methylene groups of methylene linkages would be expected to absorb [27].

Tomita and Ono [28] invetigated the random chemical structures of melamine-formaldehyde resins including methylated melamine-formaldehyde resins and urea-melamine formaldehyde resins by Fourier Transform ^{13}C-NMR spectroscopy. They assigned all the combined formaldehydes, methylol and methylene ether groups, methylene structures, and dimethylene ether structures. Further information on NMR spectroscopy and the assignment of various structures can be obtained from the papers by Ebdon et al [27], Tomita et al [29], Slonim et al [30], Duclairoir et al [31] and Chiavarini et al [32].

For the resin, Type A, under investigation only methylene ether bridges were found using ^{13}C NMR spectroscopy. This is described in the next section. The following mechanism for the condensation forming methylene ether bridges has been proposed as a result of this work, by analogy with Berge [23].



$$(1)\quad -\underset{|}{N}-CH_2OH + H^+ \rightleftharpoons -\underset{|}{N}-CH_2\overset{H^+}{O}H$$

$$(2)\quad -\underset{|}{N}-CH_2\overset{H^+}{O}H \rightleftharpoons -\underset{|}{N}-CH_2^+ + H_2O$$

$$(3)\quad -\underset{|}{N}-CH_2^+ + HOCH_2-\underset{|}{N}- \rightleftharpoons -\underset{|}{N}-CH_2-\overset{H^+}{O}-CH_2-\underset{|}{N}-$$

$$(4)\quad -\underset{|}{N}-CH_2-\overset{H^+}{O}-CH_2-\underset{|}{N}- \rightleftharpoons -\underset{|}{N}-CH_2-O-CH_2-\underset{|}{N}- + H^+$$

The carbonium ion reacts in the rate determining step with a methylol group leading to the formation of a methylene ether link.

2.3.2.2 Evidence for the Absence of Methylene Bridges

The literature discussed in the above section cannot be directly used for the process under investigation as the reaction conditions used in this work differ in some way from those used previously.

Two samples of the resin under study, an intermediate sample taken before the acid catalyst addition and a final resin sample, were analysed by Dr. John Ebdon, a lecturer in the Chemistry Department of the University of Lancaster. ^{13}C-NMR spectra of, these two samples were run on the undiluted sample on 20 MHz spectrometer with a sufficient delay between pulses (20 seconds) to allow full relaxation of all carbon atoms. The spectra are given in Figure 2.3 and Figure 2.4. The ^{13}C-NMR spectrums of the final resin sample was also run in perdeuterio-dimethylsulfoxide (d6-DMSO) solvent to improve the resolution.

De Breet et al [24] and Tomita and Ono [28] showed that peaks for methylene bridges should be in the range between 47 and 58 ppm. The ^{13}C-NMR analysis reported here showed that there are no peaks in this range. This showed that there are no methylene bridges in the resin under investigation. The ^{13}C-NMR analysis also showed that there are methylene ether bridges in the resin under study based on peaks between 68 to 75 ppm. The resolution using an undiluted sample is poor in this range. The range was somewhat better resolved by running the spectra on samples disolved in d6-DMSO solvent. This is been shown for the final resin in Figure 2.5.

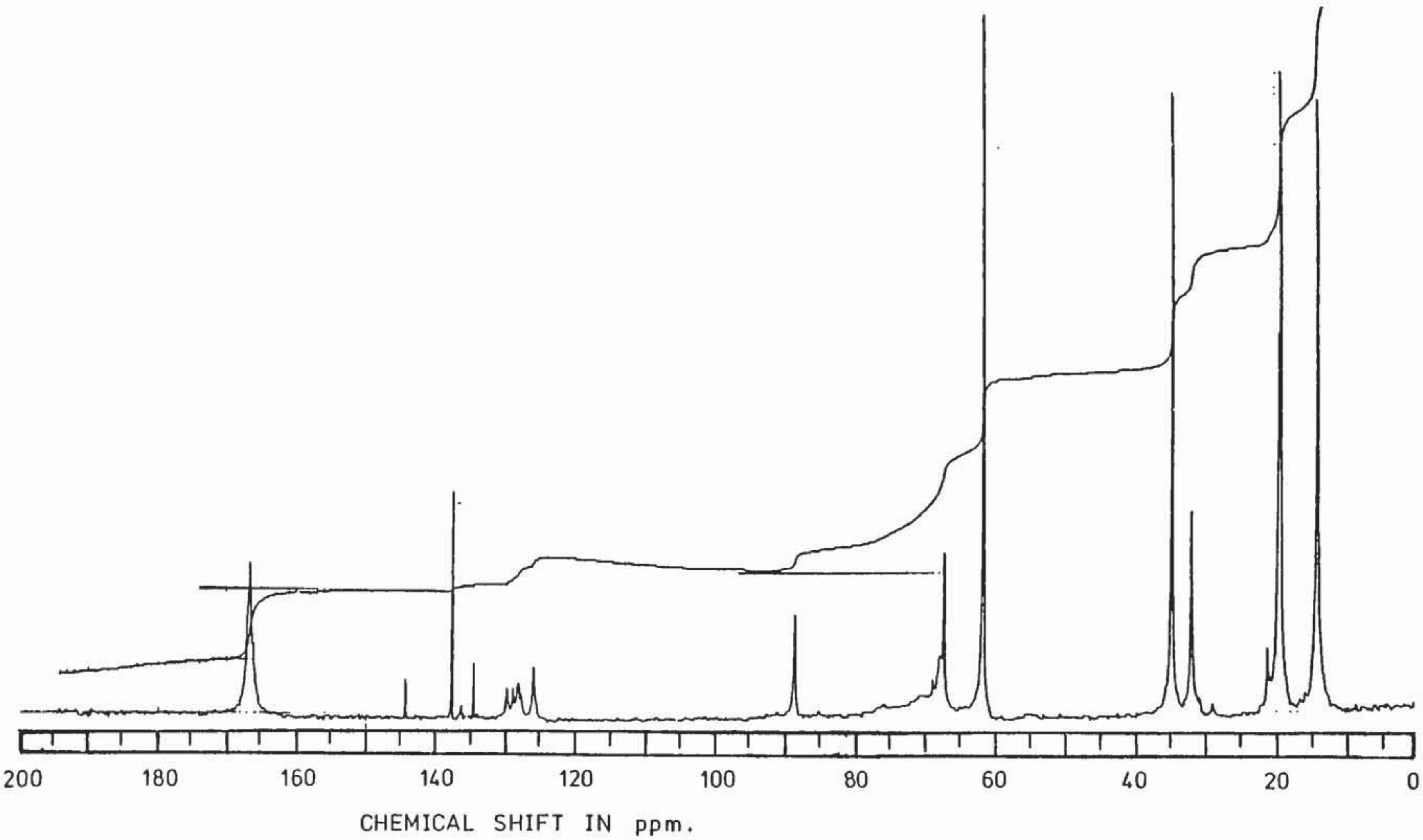


Figure 2.3 ^{13}C NMR Spectrum of an Intermediate Sample

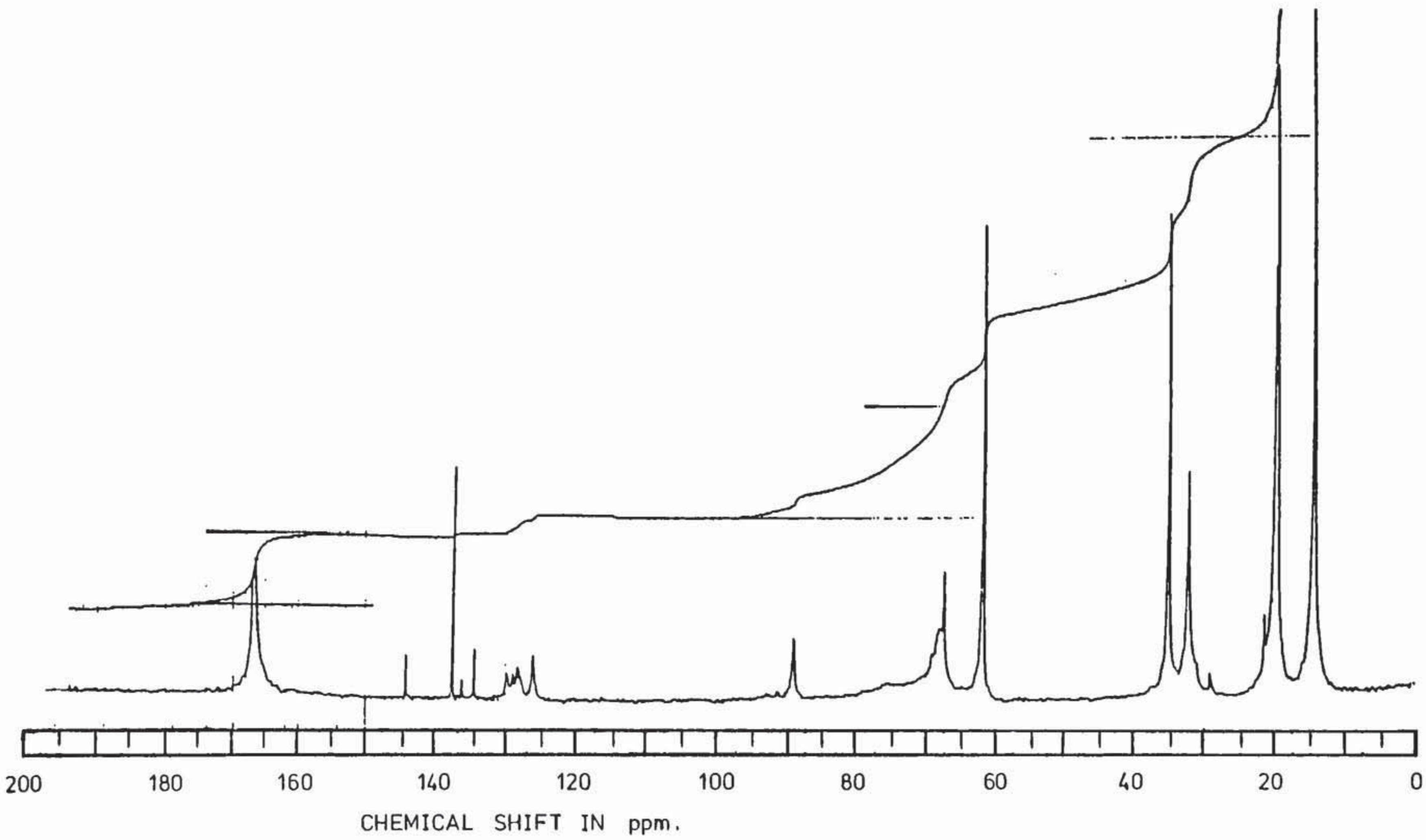


Figure 2.4 ^{13}C NMR Spectrum of a final Resin

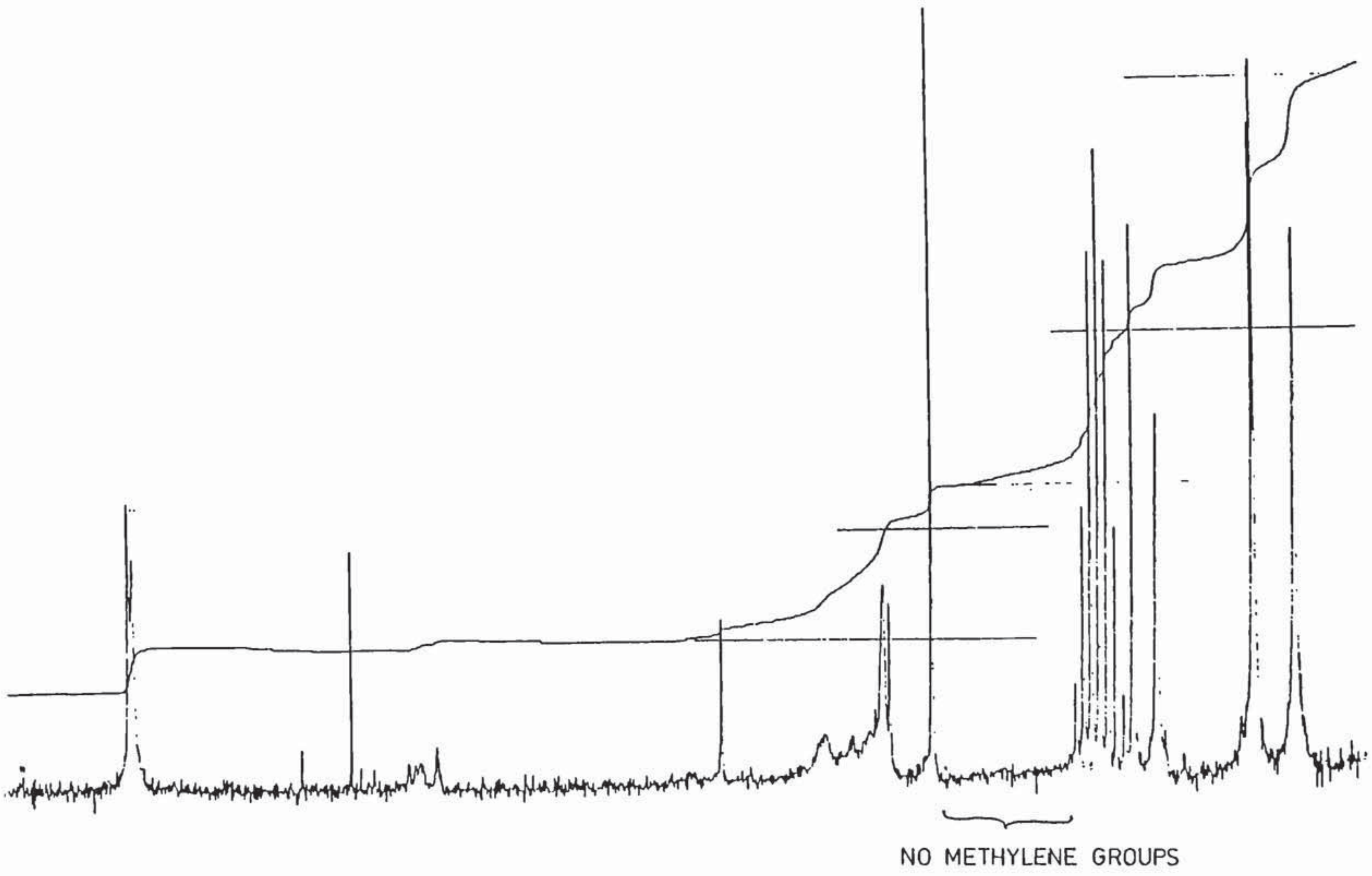
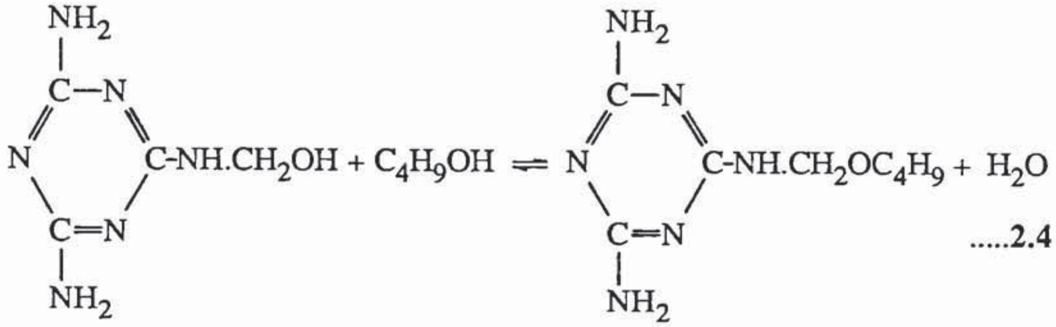


Figure 2.5 ^{13}C NMR Spectrum of a final resin run on d6 DMSO

2.3.3 Butylation Reaction

This reaction is the etherification in which the methylol groups ($>NCH_2OH$) of the methylol melamines already formed by the addition reaction react with butanol to produce butyl ether groups ($>NCH_2OC_4H_9$) and water. The reaction scheme is shown in equation 2.4.



.....2.4

Etherification of the methylol group is necessary to make the resin product compatible with other film-forming polymers during its end use and to give sufficient storage stability.

For the process under investigation both the condensation and butylation reactions take place simultaneously after the completion of the addition reaction already described. These two reactions must take place in the correct balance to produce a product with the required specification. The correct process conditions must be maintained to ensure this. The extent of methylolation, pH of the solution and the butanol concentration are the main factors influencing the balance. Butanol acts as both solvent and reactant.

Both the condensation and butylation reactions produce water. Water is also present in the formalin. It is essential to remove the water from the system, as the butylation is an equilibrium reaction which may move backwards if the water content of the system is too high. The water is removed by boiling the reactants.

For the resin under consideration, the degree of butylation achieved was found to be 2.17. This means each melamine molecule had on average 2.17 butyl ether groups attached. This result is derived from the mass balance analysis described in Chapter 5.

2.3.3.1 Literature on the Butylation Reaction

There is hardly anything published on this reaction. Only one paper by Motoyama and Uchida [33] was found about the etherification of melamine-formaldehyde resins with iso-butanol. The process conditions used were different from that of the process under study. Therefore the paper has not been discussed here. The following mechanism for the butylation reaction forming butyl ether groups has been proposed as a result of this work. This is by analogy with Berge [23].

$$(1)\quad -\underset{|}{N}-CH_2OH + H^+ \rightleftharpoons -\underset{|}{N}-CH_2\overset{H^+}{O}H$$

$$(2)\quad -\underset{|}{N}-CH_2\overset{H^+}{O}H \rightleftharpoons -\underset{|}{N}-CH_2^+ + H_2O$$

$$(3)\quad -\underset{|}{N}-CH_2^+ + C_4H_9OH \rightleftharpoons -\underset{|}{N}-CH_2-\overset{H^+}{O}-C_4H_9$$

$$(4)\quad -\underset{|}{N}-CH_2-\overset{H^+}{O}-C_4H_9 \rightleftharpoons -\underset{|}{N}-CH_2-O-C_4H_9 + H^+$$

The carbonium ion reacts in the rate determining step with butanol leading to the formation of a butyl ether group.

2.4. WATER REMOVAL

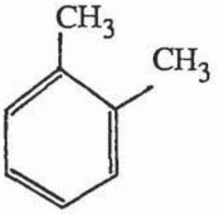
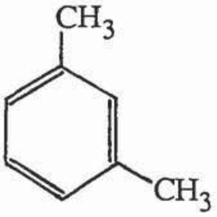
Water is removed from the reacting mixture by distillation. When boiling occurs the vapour contains a different concentration of the solvents and water from that present in the liquid reacting mixture. Butanol and water form a minimum boiling point azeotrope having a composition outside the mutual solubility range of the two liquids. A vapour-liquid equilibrium curve and a boiling point - composition curve for the n-butanol-water system [34] are given in Appendix 1.

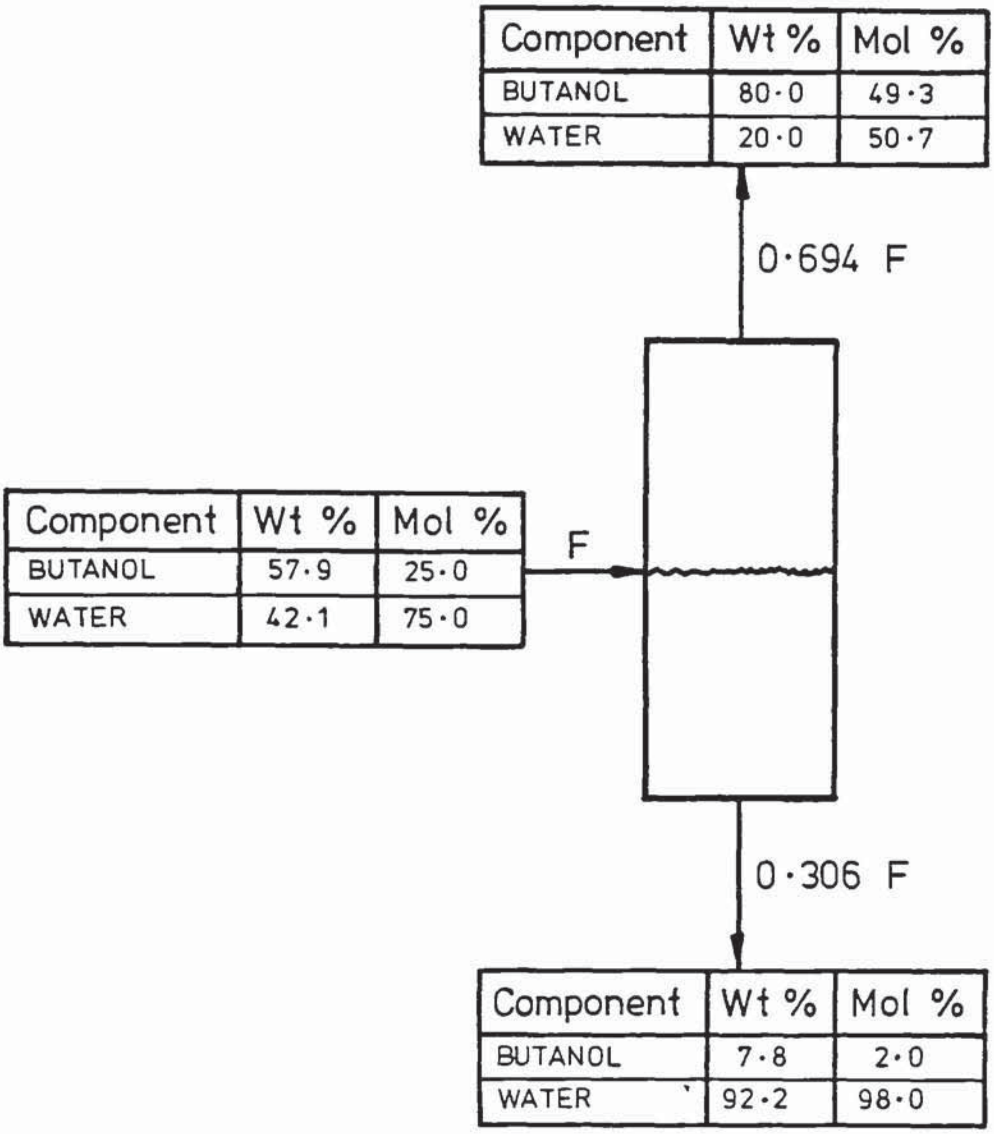
On condensation the azeotropic vapour mixture forms two immiscible liquid phases with the top phase being mainly solvent and the bottom phase mainly water. The aqueous phase is removed from the system whereas the solvent phase is returned to the reactor as the butanol is required by the reacting mixture. The equilibrium separation data for the n-butanol-water system has been presented in Figure 2.6.

For the process under investigation Xylol, a commercial mixture of the three isomers of xylene, is used as an entraining agent to improve the efficiency of the separation of the two liquid phases. The structures of the isomers are shown in Table 2.4. Xylol does not take part in the reactions and it does not dissolve in the aqueous phase. Thus it recirculates through the reactor system. The reactor xylol content therefore remains constant during the reaction and thus only one initial charge is required. With the xylol present in the system, a different equilibrium occurs between the solvent and aqueous phases as shown in Figure 2.7 [35].

It can be seen from Figures 2.6 and 2.7 that the quantity of water in the aqueous phase of the system without xylol is slightly less than that of the system with xylol. The decrease is too small to be considered significant. This shows that xylol has small influence on the separation of two liquid phases. The separation can be enhanced with KnitMesh DC packings [36]. Plant scale experiments were carried out as part of the Teaching Company Scheme [37] to establish whether the use of xylol as a separation aid could be avoided. A batch reactor equipped with a distillation column and a separator with KnitMesh DC packings was used for this purpose. These experiments showed that xylol can be eliminated from the process without having any effect on product quality or production time.

Table 2.4 Xylol Constituents

Compound	IUPAC Name	Chemical Structure	Mol. Wt.
o-Xylene	1, 2-dimethyl benzene		106.16
m-Xylene	1, 3-dimethyl benzene		106.16
p-Xylene	1, 4-dimethyl benzene		106.16



Component	Wt %	Mol %
BUTANOL	80·0	49·3
WATER	20·0	50·7

Component	Wt %	Mol %
BUTANOL	57·9	25·0
WATER	42·1	75·0

Component	Wt %	Mol %
BUTANOL	7·8	2·0
WATER	92·2	98·0

F = mass flow rate at 20° C.

Figure 2.6 Equilibrium Separation of the n - Butanol / Water System

Illustration removed for copyright restrictions

Figure 2.7 Equilibrium Separation of the n-Butanol / Xylol / Water System [35]

CHAPTER THREE

BATCH PRODUCTION OF COATING RESINS

3.1 INTRODUCTION

This chapter deals with the commercial batch production of coating resins. This includes the description of the production plant, the batch process and the process control and product testing employed during the coating resin manufacture at BIP. The basic chemistry was discussed in Chapter 2 and it was seen there that a wide range of different product can be produced by varrying different parameters. Hence the production plant under consideration is a typical multi-product batch plant. It was also seen in Chapter 2 that some solvent goes out of the reactor system with the aqueous phase. This solvent is recovered in a separate solvent recovery plant. Some information on this recovery plant has also been included in this chapter.

3.2 PRODUCTION PLANT

The production facility under investigation by the Teaching Company consisted of number of identical stainless steel reactors with variations in overhead equipment. Some have only a vapour riser, condenser and separator whilst others have a distillation column to fractionate the returning wet solvent phase from the separator.

The batch reactor system considered in detail for this work is shown in Figure 3.1. It is a typical reactor system consisting of a reactor, distillation column, condenser and a buffer tank. The reactor is fitted with heating or cooling jackets and coils where steam at 3.5 bar is used as the heating medium. It is provided with stirring by a turbine agitator.

The distillation column is a packed column on top of the reactor. The rising vapour from the reactor is contacted directly with the wet solvent returned from the separator via the buffer tank and the operation is effectively a batch distillation with the reactor acting as the reboiler.

The distillate from the column is condensed in the condenser, which is a vertical shell and tube heat exchanger where water is used as the cooling medium. The condensate can be directed either to a buffer tank, which overflows to the reactor, or a separator, where it separates into two phases, the upper phase a wet solvent phase and the lower phase an aqueous phase known as aqueous distillate. The separator is provided with DC KnitMesh packings [36] to increase the separation efficiency.

The wet solvent overflows from the separator to the buffer tank. It can either be removed from the system, or returned to the reactor. The return can be directly by an overflow from the buffer tank, or via the column as reflux. When the wet solvent is used as reflux to the column, the reflux flow rate is controlled by the column top temperature, which is set to maintain the azeotrope composition at the top of the column. When it is not possible to maintain this condition because the reflux rate required is more than is available, the control is switched to control the buffer tank level and all the wet solvent is returned as reflux. This occurs in the later stages of the reaction.

The aqueous distillate from the separator is pumped and metered either directly to a storage tank or via an intermediate weigh tank provided with load cells. The aqueous distillate flow rate is controlled by a level controller on the separator interface level.

The process also requires a blender and a plate and frame filter press which

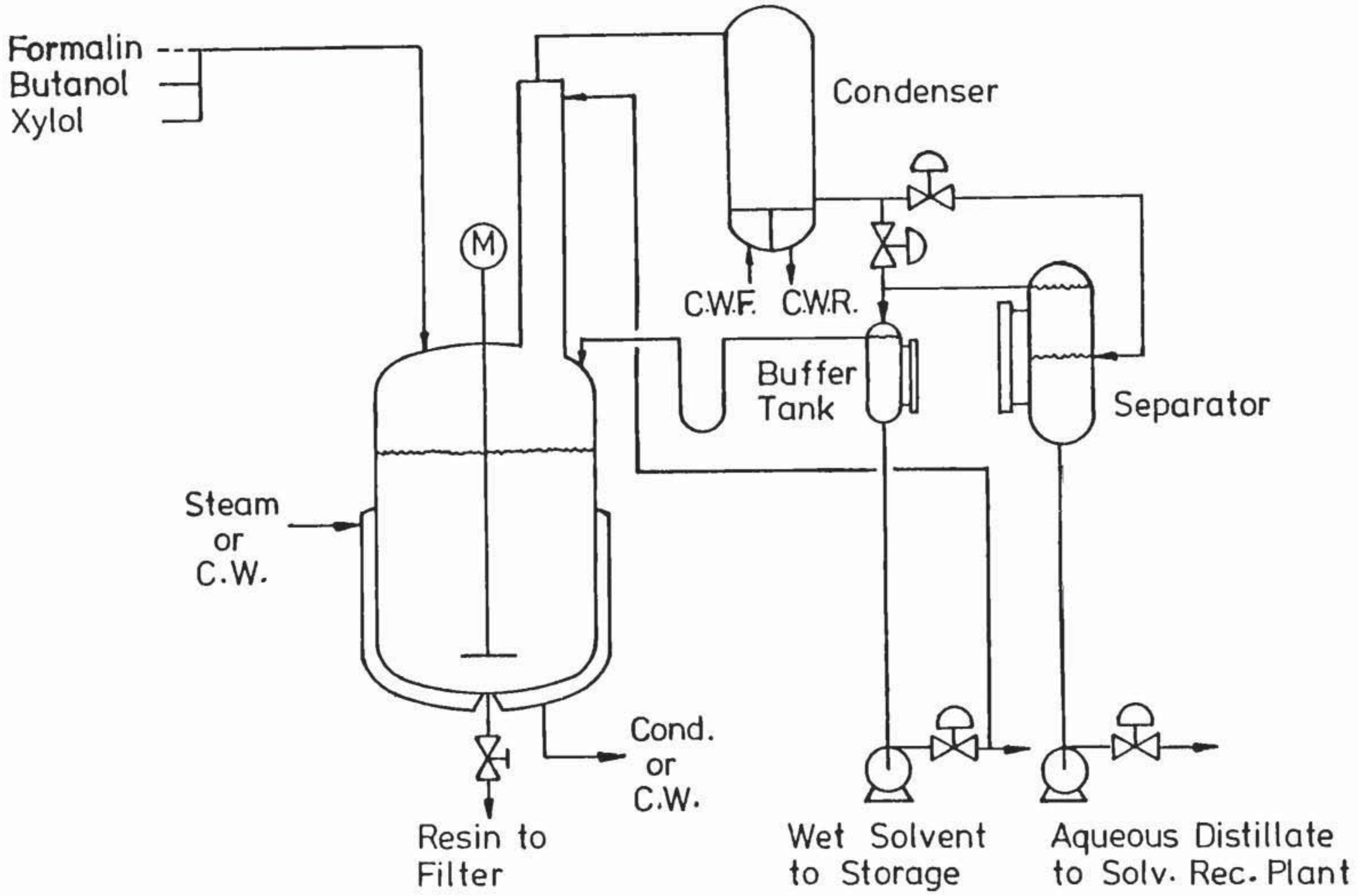


Figure 3.1 Coating Resin Batch Reactor

are not shown in Figure 3.1. The solvent recovery plant has been described in Section 3.5.

3.3 BATCH PROCESS

The coating resin manufacturing process is divided into six distinct stages, each having a specific control method. These stages are; charge preparation, methylolation, dehydration, acid reaction, solvent adujustment and the finishing stage. These names were given during this research work. Originally the names used for these stages were different in some cases. The methylolation stage was known as an alkaline boil stage, the acid reaction stage was known as an etherification stage, the solvent adjustment stage was known as a vacuum stripping stage and the charge preparation stage was known as two stages, an initial charge stage and a pH adjustment stage.

For type A resin, these stages occupy a total cycle time of approximately 19 hours. It is also possible to use the recovered butanol containing some xylol and water. However, it has not been considered in the resin formulation. The raw materials are given in Table 3.1. Each stage has been described in the following sub-sections.

Table 3.1 Raw Materials

Melamine
Formalin (44%)
n-Butanol
Xylol
Acid Catalyst

3.3.1 Charge Preparation

The volumetrically specified quantities of n-butanol and 44% formalin are charged to the reactor by pumping them from the storage tanks. The mixture is stirred.

A sample is withdrawn from the reactor and tested for pH. In order to adjust pH of the reactants within the range 5.8 - 6.3, sodium hydroxide or formic acid is added to the charge.

When the pH is adjusted within the specified range, the specified quantity of melamine is charged to the reactor.

3.3.2 Methylolation

After checking that all the atmosphere vents are open, agitation is started and heat applied by starting steam through the reactor jackets and coils. The mixture is brought to the boil and refluxed for a period of fifteen minutes returning all the process distillates back to the reactor.

Methylolation is the process stage from the beginning of the heat application to the completion of the total reflux period. The reaction temperature rises from around 25 °C to 95 °C which is the boiling point of the mixture. During this stage the addition reaction takes place between the melamine and formaldehyde as described in Section 2.4.1. This stage generally lasts for 40 - 60 minutes.

3.3.3 Dehydration

The volumetrically specified quantity of xylol is charged to the reactor and the water removal is started. This is done by directing the process distillates to the separator from where the top, solvent phase, is recycled back to the reactor via the buffer tank whereas the bottom, aqueous phase, is continuously removed from the system as an aqueous distillate, as described in Section 3.2.

As the water removal process proceeds, the condensation and butylation reactions occur simultaneously and begin to form the synthetic resin. During this stage the free water, which enters the reactor with formalin, and recovered butanol if used, and the water of reaction is distilled out of the system.

A further charge of butanol, normally termed butanol (2), is made three hours into the dehydration stage.

The temperature of the reacting mixture is used as the control parameter for this stage. The stage ends when the temperature of the reacting mixture reaches 102 °C. This temperature corresponds to the removal of most of the water, as the boiling point of the reaction mixture changes with its composition. The boiling point-composition data given in Appendix 1 for a water-butanol system may be used as a rough guide. The stage generally lasts for four to six hours.

3.3.4 Acid Reaction

The acid catalyst is added to the reactor. This is the starting point of the acid reaction stage. Heating is gradually reapplied and the water removal process continued. This water removal process is slightly different from that used in the dehydration stage. The distillation column is used to further enhance the water removal. This is done by refluxing the solvent phase, as described in Section 3.2.

Both the condensation and butylation reactions occur simultaneously during this stage and the reacting mixture becomes more viscous. The reacting resin is tested hourly during this stage for viscosity and solvent tolerance (see Section 3.4) to monitor the extent of these reactions. The resin viscosity is controlled within certain limits by the addition of n-butanol or the removal of wet solvent from the reactor.

When the solvent tolerance of the resin is within a specified range, the chemical process is considered to be complete. The reaction temperature rises from 102 °C to 120 °C, during the stage. Almost all the water is removed from the reactor. Cooling is applied to reduce the reactor temperature for the next stage which is final resin adjustment.

3.3.5 Solvent Adjustment

When the resin is cooled to an appropriate temperature, 60 °C, all the vent valves are closed and vacuum is applied to the reactor. Heating is applied in such a way that the distillate temperature does not exceed a specified value. The wet solvent is removed from the system during this stage, until the viscosity is within the final specified range. When this viscosity is achieved, vacuum and heating are stopped and the stage is completed. By control of the viscosity, the solids content of the resin can be adjusted to the required specification provided the chemical properties of the resin are in balance.

3.3.6 Filtering, Blending and Packaging

This is the finishing stage. The resin is filtered through a plate and frame filter press to remove insoluble material and any gelled particles and then pumped to a blender where, if necessary, further solvent adjustments can be made. The product with the final required specification is drummed off for shipment.

3.4 PROCESS CONTROL AND PRODUCT TESTING

Three control tests are performed while the resin is being processed. These are, pH, bubble tube viscosity and solvent tolerance. Density is used as a process control parameter for the solvent adjustment stage. This is discussed in Section 3.6.

Once the process is complete, the resin is sampled and the accepted finished product tests are performed on it. These quality control tests are; cone and plate viscosity, solvent tolerance, oven solids content or density, acid value, colour, clarity and application tests are performed on a panel coated with resin and paint containing resin. The application tests are carried out to check the resin's physical properties when made up and used as a coating finish. The film should be clear with no haze or opalescence and free of striation.

Some of the control tests have been described in the following sub-sections.

3.4.1 Viscosity (PRS Bubble Tube)

During the acid reaction stage of the resin manufacturing process, viscosity of the resin solution is measured at hourly intervals. A simple method, a set of standard Paint Research Station (PRS) bubble tubes, is employed to measure viscosity.

An empty clean PRS bubble tube is filled up to the mark with the resin to be tested. It is then sealed and placed in a water bath at 25 °C ± 0.5 °C for at least 30 minutes along with the standard PRS bubble tubes. The sample tube and one of the standard tubes are taken out of the bath and inverted together, to compare the rate of bubble travel in both. The PRS tubes are numbered and the PRS viscosity of the resin is quoted as the number on the standard tube which has an equivalent rate of bubble travel.

3.4.2 Viscosity (Ferranti-Shirley, Cone and Plate)

The viscosity of the finished resin product is determined by means of a Ferranti-Shirley Cone and Plate viscometer. This is a more precise method which provides a higher degree of accuracy than the PRS method.

A sample of resin is sheared at a constant rate between a rotating cone and a stationary plate. The transmitted torque is measured and used to calculate the resin viscosity. Both the cone and plate are kept at a constant temperature by circulating water through them from a thermostatically controlled water bath. The viscosity is calculated and expressed in poise.

3.4.3 Solvent Tolerance

This test is performed on the resin solution at hourly intervals, during the acid reaction stage of the process. The finished resin sample is also tested by this same method which is a simple titration. A standard 5g quantity of resin is titrated with white spirit at 20 °C until the resin will no longer dissolve and the solution is cloudy.

The solvent tolerance is thus expressed as 'ml' of white spirit tolerated by 5 gram resin at 20 °C. It is possible for commercial white spirit to be deficient in aromatic content leading to erroneous test results. The white spirit can therefore be checked by comparison with a standard solvent consisting of a mixture of 98% heptane and 2% toluene and adjusted using industrial methylated spirits.

3.4.4. Oven Solids Contents

The solids content of the finished resin, as measured by the oven solids test method, is required to be within a certain specification range. This test has now been superseded by the density test described in Section 3.4.5 as a result of the research work carried out by Freeman for the Teaching Company Scheme [1], which showed that the new test was quicker and more accurate. There are many variations of the oven solids test performed in industry and the test results will vary depending on the particular test adopted. The BIP method is a variant of the British Standard test BS2782 part 1, 1970 method 107E, and described in Appendix 3.

3.4.5 Density

The Anton Paar DMA46 digital density meter is used to measure the density of the finished resin. This meter can measure density to four decimal places with a quoted accuracy of ± 0.0001 g/cm^3.

The principle of operation is that a cell of fixed volume at a controlled, constant temperature is electromagnetically excited causing it to vibrate at its natural frequency which is dependent upon the density of the material contained in the cell. Once the sample cell is filled with a sample of material, the sample density is determined precisely by the measurement of the period of oscillation of the sample tube. The determination is unaffected by viscosity, volatility and surface tension but the sample must be representative of the batch from which it came and be totally free of air bubbles.

3.4.6 Acid Value

The acidity of the finished resin sample is measured by an acid value titration and expressed as miligrams (mg) of potassium hydroxide required to neutralise one gram of resin.

3.5 SOLVENT RECOVERY

It has been shown in the description of the batch process that not all the butanol used as a raw material remains in the resin product. Some of it leaves the system with the aqueous distillate stream during the process and some leaves with the vacuum stripped solvent, which is removed from the reactor during the solvent adjustment stage. Butanol is recovered from these two sources and recycled as a raw material.

The vacuum stripped solvent is of such a composition that it can be used directly in resin production. However the aqueous distillate needs further processing in a solvent recovery plant before it is suitable for reuse, as it contains only 8% butanol.

The solvent recovery plant can be described very briefly as follows. Aqueous distillate is a multicomponent liquid containing water, butanols, methanol and formaldehyde. In order to separate it into streams of the required quality, it has to be processed through three distinct distillation operation as shown in Figure 3.3. The same, 20 plate, bubble cap column is used for each of three distillations D1, D2 and D3. The D3 distillation operation has been proposed as a result of work done during the Teaching Company Project [38]. Only two distillations as shown in Figure 3.2 were in operation before that.

3.5.1 D1 Distillation

Aqueous distillate is fed to the fourth plate of the column (numbering from the bottom up) and distilled. The bottom product, termed weak formalin, is a water/formaldehyde solution which contains 3-6% formaldehyde. It is pumped away for use as a diluent in other plants. The top product is a water/methanol/butanol mixture and is stored in a 23000 litre 'primary' tank as feed for the D2 distillation.

3.5.2 D2 Distillation

From the primary tank feed is pumped to the 15th plate of the same column for the D2 distillation operation. Methanol is recovered in this operation, which forms the top product as a rich (95%) methanol/water solution. It is pumped to the recovered methanol tank. the bottom product is a mixture of water and butanols of about the azeotrope composition. When cooled, the bottom product settles into two phases, an aqueous phase and a solvent phase. The solvent phase containing about 80% butanols is stored in a D3 feed tank whereas the aqueous phase is recycled back to the main aqueous distillate storage tank.

3.5.3 D3 Distillation

The feed, containing 20% water in butanols, is pumped to the 15th plate of the same column for the D3 distillation operation. In this operation almost dry butanol (both iso and normal) containing about 2% water is obtained as a bottom product. It is stored in the wet iso-butanol tank, to be reused as a raw material for the iso-butylated resins. The top product consists of the butanol-water azeotrope. It is separated into an aqueous phase, which is pumped back to the aqueous distillate tank, and a solvent phase which is recycled back to the D3 feed tank.

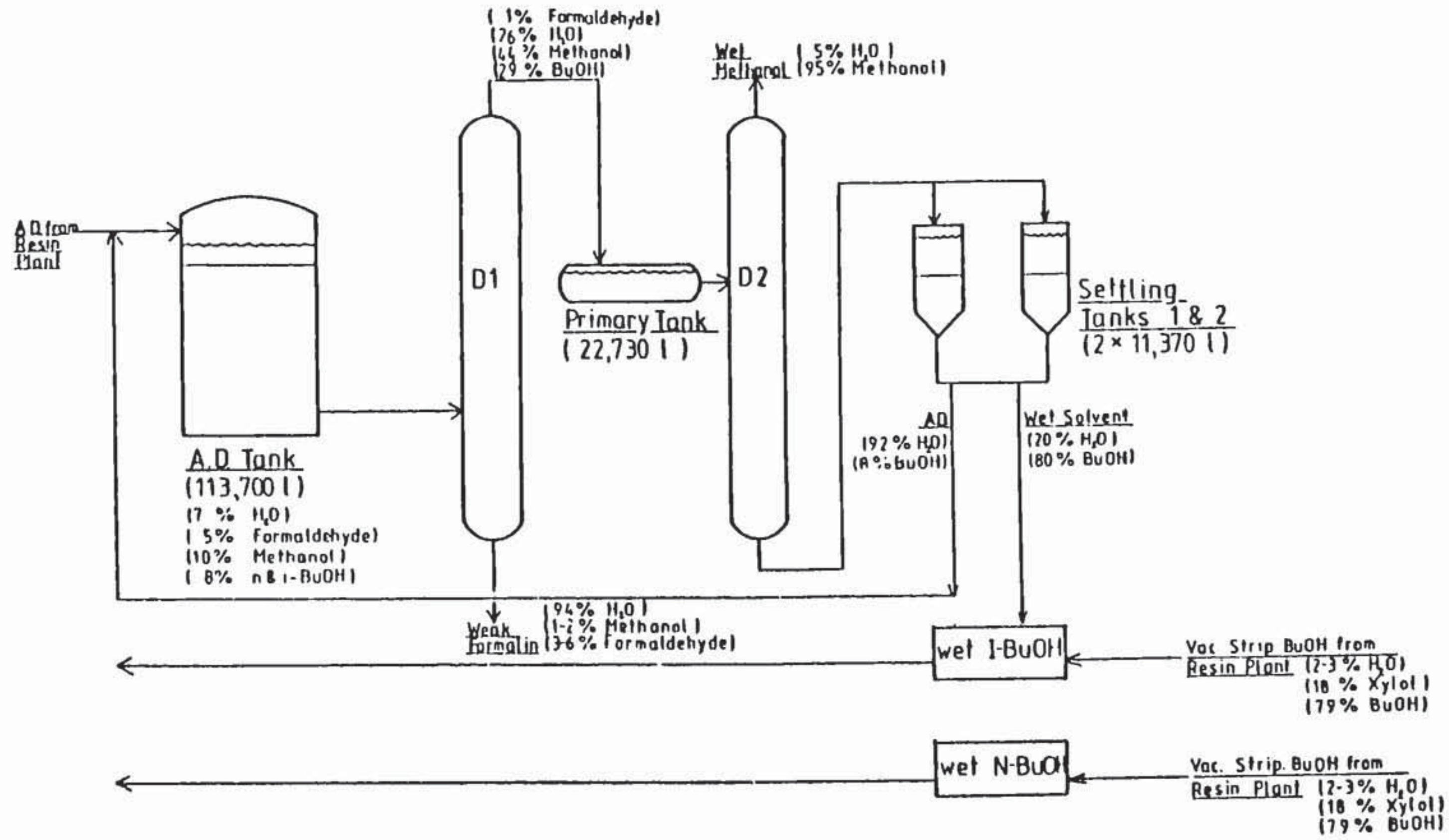


Figure 3.2 Solvent Recovery Plant Operation 1

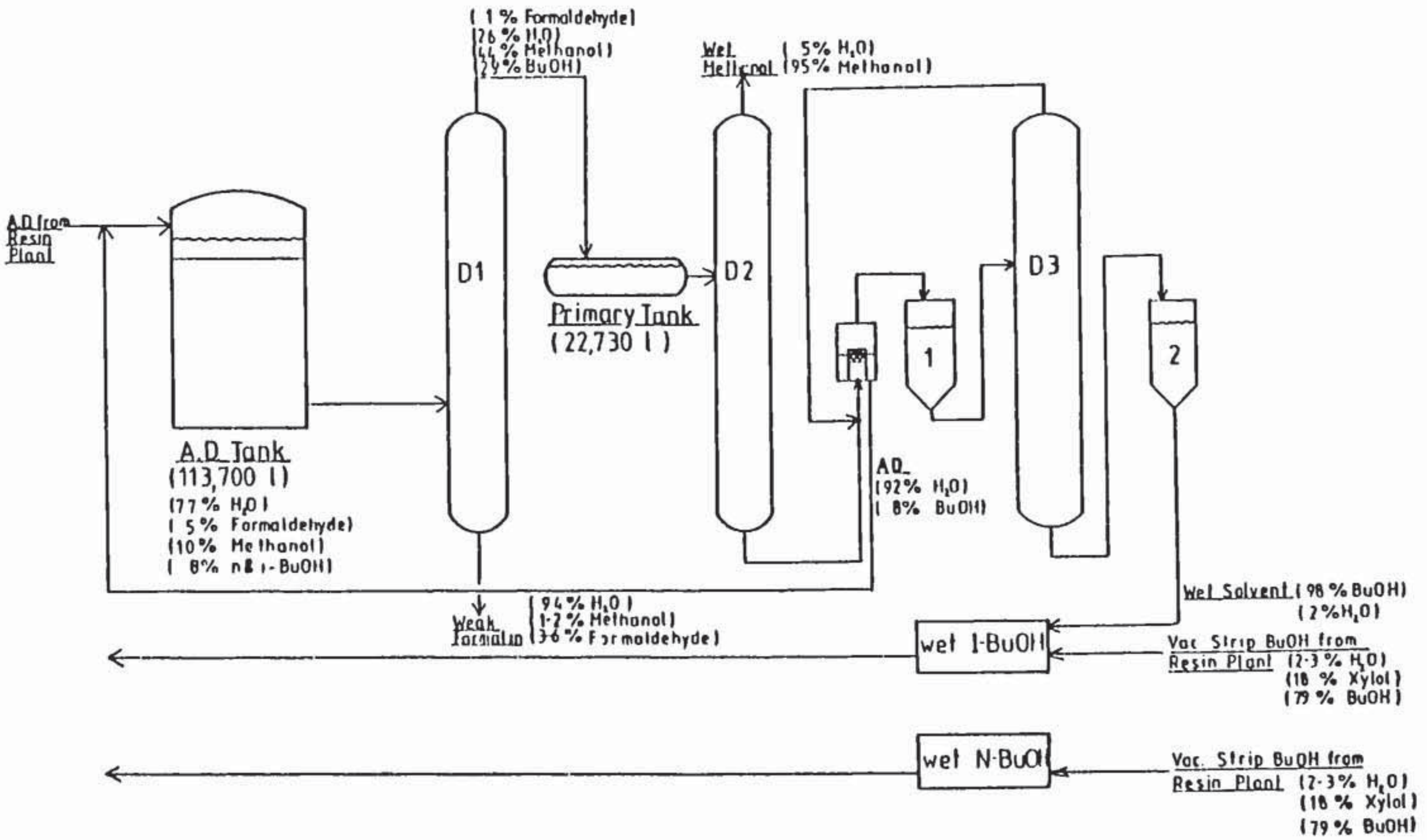


Figure 3.3 Solvent Recovery Plant Operation 2

3.6 DISCUSSION

The chemical reactions occur during the methylolation, dehydration and acid reaction stages of the process. During the methylolation stage the addition reaction between melamine and formaldehyde occurs and reaches an equilibrium. The degree of methylolation and the composition of various methylol melamines produced, are the important factors here as the further reactions depend on them. During the dehydration and acid reaction stages, it will be shown later that the condensation and butylation reactions occur simultaneously in a competitive way. These reactions must take place in a correct balance, otherwise, the resin product can be over condensed/butylated or under condensed/butylated.

The quality of resins is mainly judged by the three traditional control tests, viscosity, solvent tolerance and solids content. Viscosity increases due to polymerization, hence it is used as a measure of condensation. The solvent tolerance is considered to be a rough measure of butylation. It is also affected by the condensation [33] and the water content of the resin product [39].

Solids content of a resin is a function of all the three reactions. The 'actual solids content' is defined as the resin remaining when the solvent has been removed and expressed as percentage of the resin solution (proportion of resin to solvent). In practice, it is determined by drying a sample to constant weight under vacuum at room temperature, and generally known as 'vacuum solids content'. This test can take up to two weeks.

The oven solids test, described in Section 3.4.4, does not measure the actual solids content as the test is carried out at high temperature (120 °C) for two hours, during which further reactions take place, depending upon the reactivity of the resin. This test thus depends on the reactivity of the resin and the value obtained is always lower than the resin's actual solids content. The test itself has been shown to have a poor reproducibility [1].

The oven solids test has now been replaced by the density test. Freeman [1], a Teaching Company associate, concluded that the density of a resin is directly proportional to its actual solids content, independent of the degree of reactivity. He also correlated the density measurement with the traditional oven solids test. Thus, 5 minutes taken for the density measurement replaces the 3 hours required for the oven solids test. The measurement of density is considerably more accurate and reproducible than the oven solids test.

During the solvent adjustment stage, solvents are removed under vacuum to adjust the resin's solids content into the specified limits. In the past there was no quick test to measure the solids content. Because of the relationship between the density and the solids content, density is now used as a process control parameter for this stage.

CHAPTER FOUR

LABORATORY SCALE BATCH REACTOR SYSTEM

4.1 INTRODUCTION

The main objective of the Teaching Company Scheme was to maximise the efficiency and economy of the batch reactor process. In order to achieve this, it was decided to perform investigations into the process and to study the chemical reactions involved and the control parameters of the process. It was not practical to carry out all the chemical process investigations on the full scale batch reactor. A laboratory scale batch reactor was used for these purposes. This equipment is described in this chapter, together with the results obtained. This work showed that the laboratory tests produced similar product to the full scale plant, and were satisfactory for the study of the process.

4.2 LABORATORY SCALE PLANT

The laboratory scale batch reactor system is shown in Figures 4.1 - 4.3. A standard 5 litre, flanged quickfit reaction flask, equipped with an electric heating mantle and an anchor stirrer, was used as a batch reactor.

The production process described in Chapter 3 was simulated as closely as possible. All the raw materials used in the laboratory preparations were taken from production stock and they were used in proportion according to the standard formulation.

The reactor system as shown in Figure 4.1 was used for the charge preparation and methylolation stages. For these stages a single, vertical condenser was used as an overhead equipment, as all the process distillates were to be returned to the reactor during the total reflux period of the methylolation stage.

At the start of the dehydration stage, the single condenser was replaced by the specialised overhead equipment shown in Figure 4.2. This system was used for the dehydration and acid reaction stages. The overhead equipment was designed to simulate as closely as possible that on the production plant. The vapour riser was not packed. It had a vacuum sealed jacket around it to reduce vapour condensation within it. The vapour was condensed in a single pass, tube in shell, heat exchanger and fell by gravity into a separator where it separated into two phases. The lower, aqueous phase was decanted from the system as an aqueous distillate. The upper, solvent phase (termed wet solvent) overflowed into a U-trap and then back to the reactor. The U-trap was provided with a valve, from where the wet solvent could be removed from the system, if required.

The reactor system as shown in Figure 4.3 was used for the solvent adjustment stage, or vacuum stripping operation, described in Section 3.3.5. The filtration stage as described in Section 3.3.6 was omitted from this laboratory resin production process.

4.3 EXPERIMENTAL WORK

Experimental work reported in this thesis is divided into two parts. The first part consists of the experimental work carried out in the early stages of the Teaching Company Scheme to establish the validity of the bench scale experiments. This work is discussed in this chapter. The second part consists of the experimental work which was carried out later to study in detail the chemical reactions occurring during the process. This will be discussed in Chapter 6.

The primary objective of the early experimental work was to establish whether

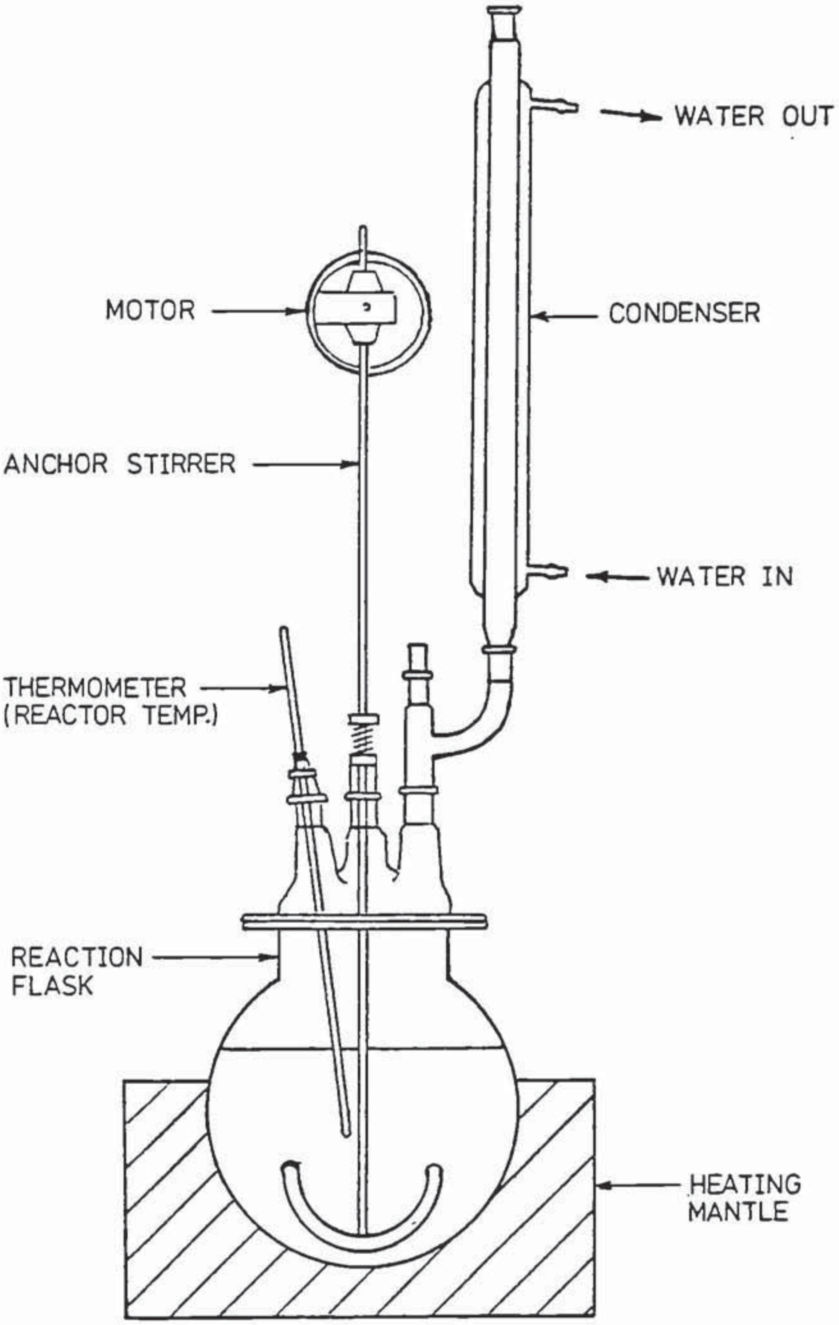


Figure 4.1 Laboratory scale batch reactor for the Charge preparation and Methylolation Stages.

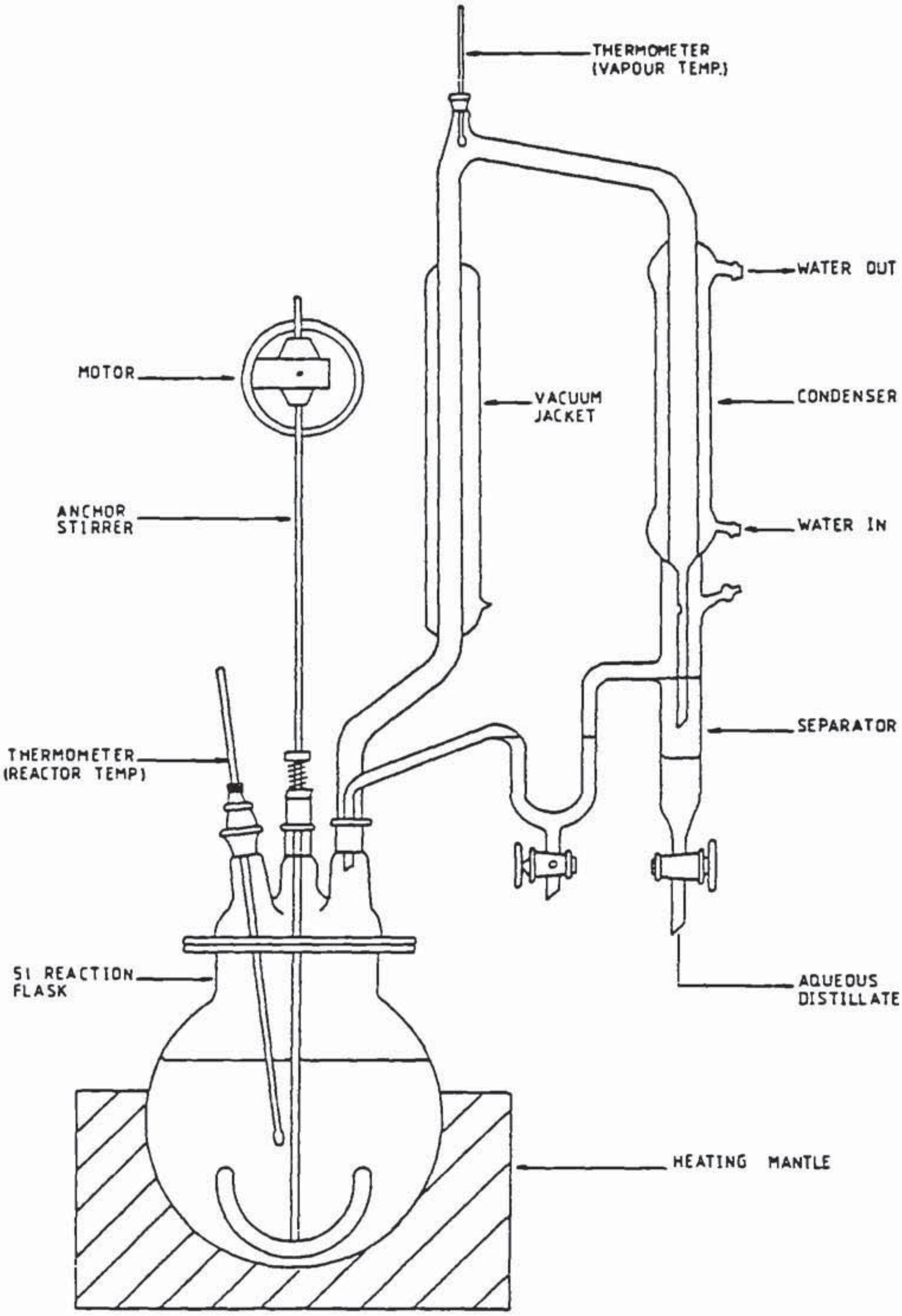


Figure 4.2 Laboratory scale batch reactor for the Dehydration and Acid Reaction Stages.

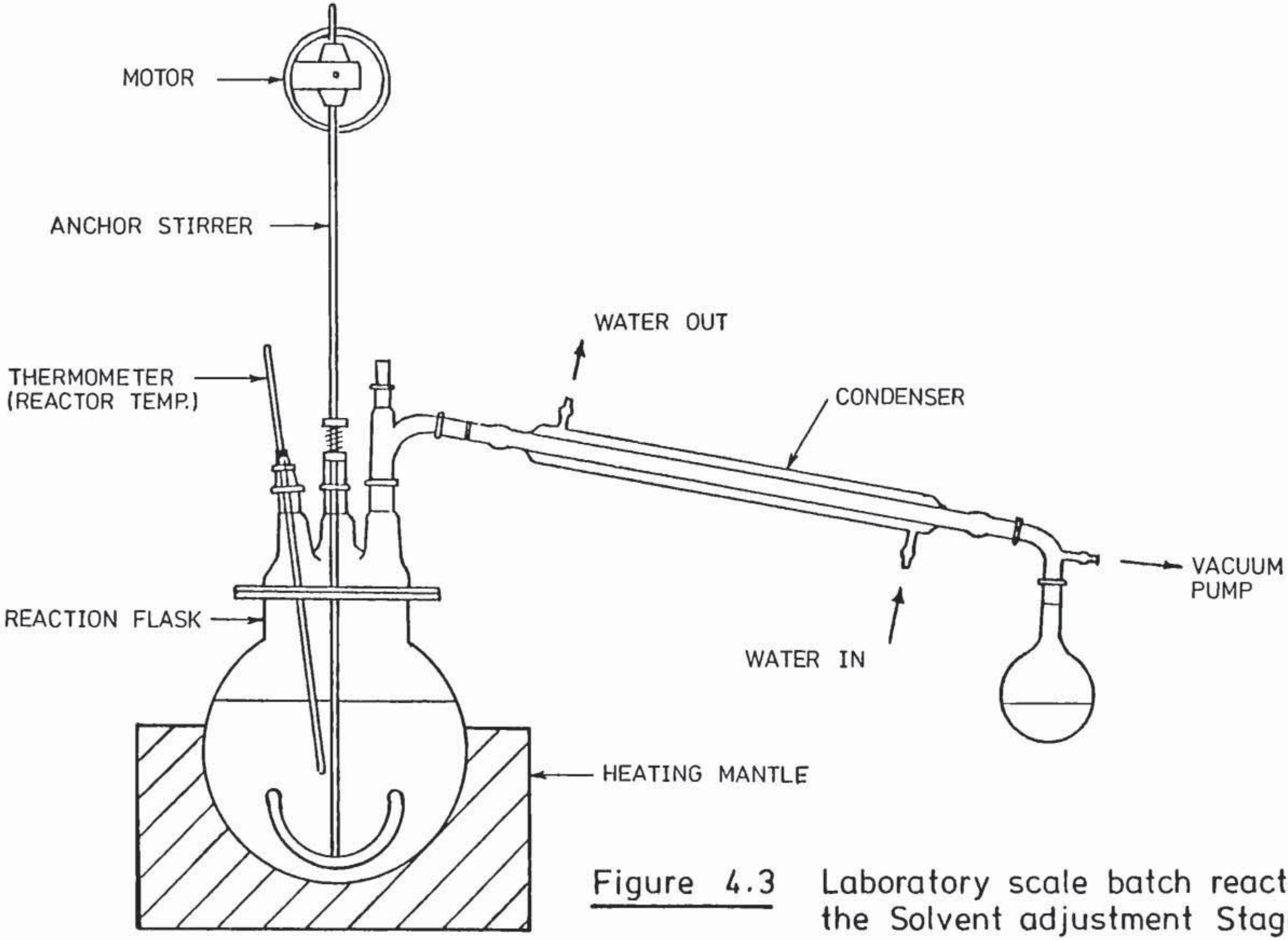


Figure 4.3 Laboratory scale batch reactor for the Solvent adjustment Stage.

the process plant could be simulated by the laboratory scale to produce resins with the specified quality. At the same time, the secondary objectives were to gain experience and understanding of the resin making process using the existing control parameters and at the same time to carry out some initial investigations into new control parameters. A series of 9 experiments were performed on the laboratory scale. Each experiment was given a "PV" code number.

The first three experiments, PV1 - PV3 , were familiarisation exercises when all the production procedures and control tests procedures were commissioned. They were useful in determining an appropriate size of batch charge for a 5 litre reactor. Different batch sizes were tried during these experiments. The melamine charges for these experiments PV1 - PV3 were 504, 756 and 680 grams respectively. The melamine charge of 680 grams was found to be an appropriate one and the raw material formulation based on this charge was used for the experiments which were carried out subsequently.

In experiments PV8 and PV9 recovered butanol from previous experiments was used as a solvent charge. Pure butanol was used in all other experiments. A batch in which recovered butanol is used is termed a 'wet' batch. In the experiment PV8, vacuum stripped butanol from the batches PV1 to PV7 was used as a solvent charge whereas in the experiment PV9, an artificially made recovered butanol was used as the solvent charge. These two experiments will not be discussed in detail as the 'wet' batch method of production is out of the scope of this work. However, they are mentioned here because an important conclusion that the vacuum stripped butanol contains very little water was drawn from the experiment PV8. This conclusion was drawn from the fact that the total quantity of aqueous distillate removed was very similar to that of the previous batches despite the use of recovered solvent. This was a very important finding in connection with the production plant because, as shown in Figure 3.2, the wet n-butanol tank contains vacuum stripped solvent only, which was subsequently confirmed to contain very little water.

Details of experiments PV4 to PV7 are given in Appendix 2. Various parameters such as reaction temperature, pH, aqueous distillate volume (AD), viscosity and solvent tolerance were monitored at intervals throughout the process. Refractive Index (RI) and density (RI: PV4, 5 &7. Density: PV6 &7) were also monitored throughout the process, this study has been reported by Freeman [1] and is not discussed in this work. The resin products from these batches were tested by the Quality Control Laboratory at BIP.

4.4 DISCUSSION OF RESULTS

The results of the quality control tests are summarised in Table 4.1. It can be seen from this table that the quality of the resins produced from these batches was within the specification. Therefore, it was concluded that it is possible to simulate the process plant to produce resins with the specified quality.

Table 4.1 Results of quality control tests

Experiment No.	Oven Solids	Viscosity PSF	Solvent Tolerance	Acid Value	Result Pass/Fail
PV4	59.38	12.31	30.8	0.66	Pass
PV5	59.63	15.38	28.6	0.60	Pass
PV6	60.45	19.16	33.0	0.64	Pass
PV7	58.98	16.05	28.8	0.62	Pass
Specification	58 - 62	11.5 - 20.5	28 - 40	0.8 max	

Comparisons with the standard manufacturing method have been made in the following discussions.

4.4.1 Batch Time

The laboratory plant was found to be slightly more efficient than the works plant. This was because of its better heat input and agitation efficiency than the full scale plant. Table 4.2 shows the data regarding the reaction times involved in the three process stages during the experiments PV4 to PV7. It also contains the plant data regarding the normal reaction times for these stages. These small differences in the batch times were eliminated in the laboratory by controlling the heat input and degree of agitation. This was achieved during the second set of experiments VP1 to VP11 which will be discussed in Chapter 6. It was therefore possible to establish fixed times for the various events in the laboratory experiments. The temperature and AD profiles with respect to this schedule of events are discussed in the following sections.

Table 4.2 Reaction time involved in three stages: PV4 - PV7

Process Stage	Laboratory Plant Minutes	Works Plant Minutes
Methylolation	30-35	40
Dehydration	180-230	240
Acid Reaction	245-255	250-270

4.4.2 Reaction Temperature

During the methylolation stage, the reaction temperature rises from 27 °C to 95 °C. The reaction mixture starts boiling after 25 minutes of heat application and is allowed thereafter to boil at 95 °C for a further 15 minutes during which all the process distillates are refluxed back to the reactor.

At the start of the dehydration stage, xylol is added to the reaction mixture as an entrainer and as a result of that, the boiling point of the mixture reduces from 95 °C to 93 °C. During the dehydration stage the reaction temperature rises from 93 °C to 102 °C. The change in temperature is very small during the first three hours of the dehydration stage because the water content of the reaction mixture remains high during this period. The boiling point/composition diagram given in Appendix 1 for a water/n-butanol system shows that the temperature change is very small for the water content from 70 mol% to 40 mol%. During the acid reaction stage the reaction temperature rises from 102 °C to 120 °C. Figure 4.4 shows the typical temperature / time profile for the dehydration and acid reaction stages for the laboratory experiments. This profile fits well with the plant temperature profile.

4.4.3 Aqueous Distillate (AD)

The water, removed from the system as aqueous distillate during resin production comes from two sources. (a) Water charged with the raw materials, formalin and recovered butanol if it is used. (b) The water produced by the condensation and butylation reactions.

The total volumes of aqueous distillate removed during the experiments PV4 to PV7 varied from 1508 ml to 1544 ml giving the average quantity to be 1526 ml. During these experiments the quantity of 44% formalin used per 680 grams of melamine was 1.79 litres. The molar ratio of formaldehyde to melamine was slightly higher than that used for the plant production, 5.47 instead of 5.25. Therefore, during the second set of experiments (see Chapter 6) the molar ratio of formaldehyde to melamine was adjusted to that used for the plant production. The average quantity of AD removed was decreased from 1526 ml to 1488 ml as a result of this change. A typical aqueous distillate/time profile considering this change is shown in Figure 4.5.

It can be seen from this AD profile that during the dehydration stage the aqueous distillate was removed at a constant rate of about 300 ml/hr. During the acid reaction stage, the removal rate decreased to final value of 15 ml/hr, as the reaction mixture become further dehydrated.

The aqueous distillate volumes removed during the dehydration stage of the experiments PV4 to PV7, varied from 1160 ml to 1290 ml. This was due to the fact that temperature was used as the control parameter to indicate the end of the dehydration stage. The temperature rise at this stage is very slow so the end point can be taken at any time over a half hour period which is equivalent to 150 ml of aqueous distillate. Therefore temperature is not a reliable control parameter for this stage. It was suggested to use the AD quantity removed from the reactor as a control parameter in addition to the reaction temperature to provide batch to batch consistency in processing.

The ability to simulate the full scale plant and to produce resins with the specified quality was proved. The bench scale reactor can be satisfactorily used for the study of the process.

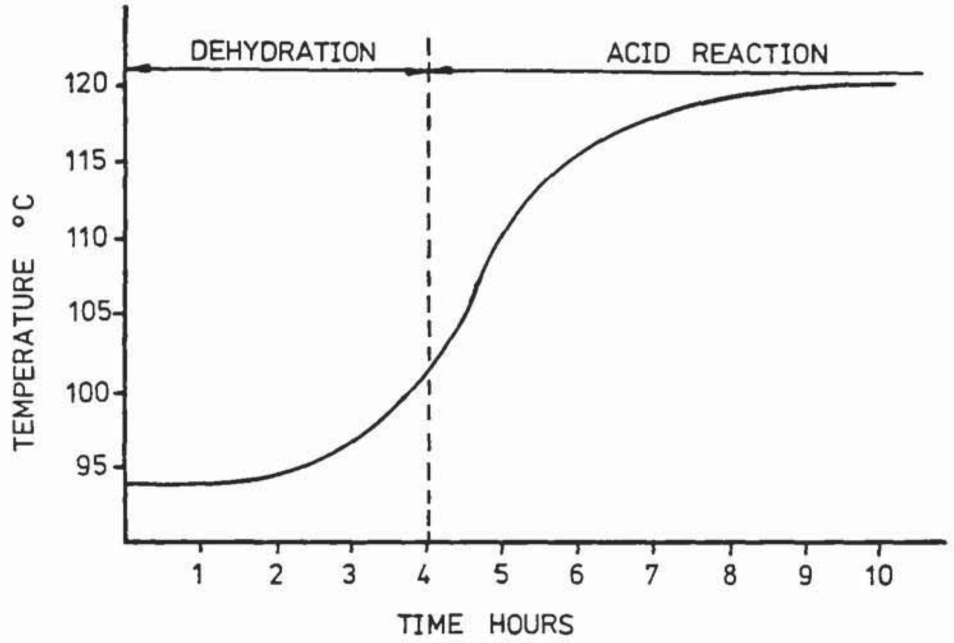


Figure 4.4 Time/Reaction Temperature Profile

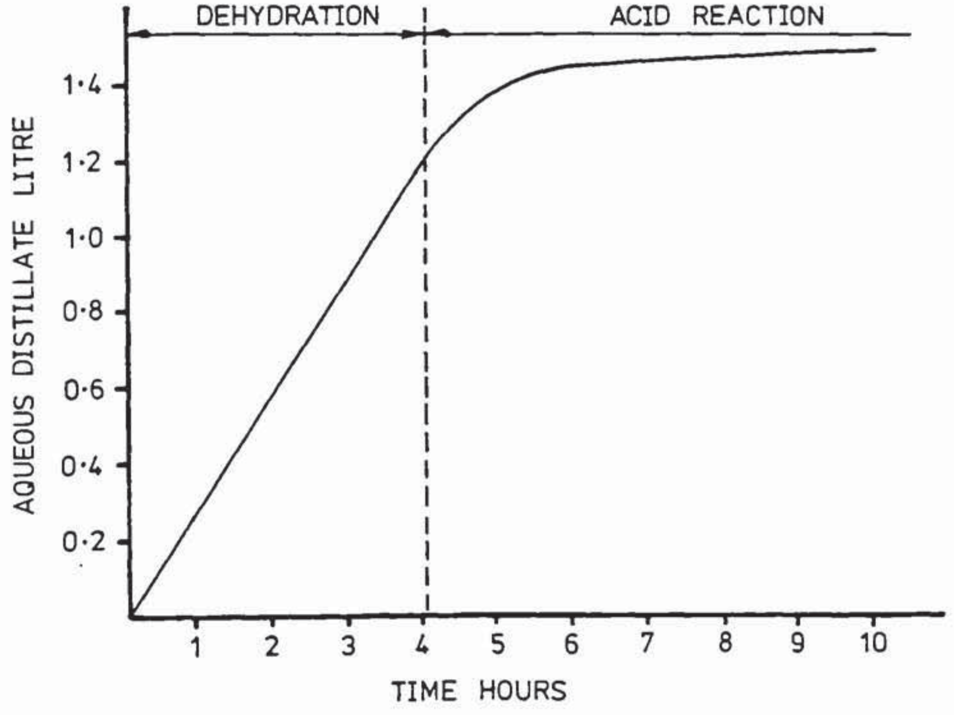


Figure 4.5 Time/Aqueous Distillate Volume Profile

CHAPTER FIVE

MASS BALANCE METHOD

5.1 INTRODUCTION

The complex chemistry involved in the resin making process was discussed in Chapter 2. During the methylolation stage, methylol groups ($-CH_2OH$) are produced due to the methylolation reaction. During the dehydration and acid reaction stages methylene ether bridges ($-NCH_2-O-CH_2N-$) and butyl ether groups ($-NCH_2OC_4H_9$) are produced by the condensation and butylation reactions respectively.

In order to study the kinetics of the reactions, it is necessary to investigate the rates of the chemical changes occurring during the process. It was possible to study the methylolation reaction on the basis of an analysis of unreacted free formaldehyde with respect to the reaction time. However, it was not possible to study the condensation and butylation reactions directly as the direct quantitative measurement of the chemical groups involved was not possible.

It was therefore necessary to devise an indirect method for studying the chemical changes occurring during the process. A mass balance method was devised for this purpose.

5.2 BASIS OF THE MASS BALANCE METHOD

The objective of the mass balance method was to collect experimental data regarding the chemical changes occurring during the process. The method was conceived from the following reaction scheme for the process:

Reaction Scheme

1. Methylolation

$$\mathrm{M\text{-}\underset{|}{N}.H} \quad + \quad \mathrm{CH_2O} \quad \rightleftharpoons \quad \mathrm{M\text{-}\underset{|}{N}.CH_2OH}$$

methylol

2. Condensation

$$\mathrm{M\text{-}\underset{|}{N}.CH_2OH} \; + \; \mathrm{HOCH_2.\underset{|}{N}\text{-}M} \quad \longrightarrow \quad \mathrm{M\text{-}\underset{|}{N}.CH_2\text{-}O\text{-}CH_2.\underset{|}{N}\text{-}M} \; + \; \mathrm{H_2O}$$

methylene ether

3. Butylation

$$\mathrm{M\text{-}\underset{|}{N}.CH_2OH} \; + \; \mathrm{C_4H_9OH} \quad \rightleftharpoons \quad \mathrm{M\text{-}\underset{|}{N}.CH_2.O.C_4H_9} \; + \; \mathrm{H_2O}$$

butyl ether

These chemical reactions were discussed in detail in Chapter 2.

It is possible to study the metyhylolation reaction by analysing unreacted free formaldehyde with respect to the reaction time. The sulphite back titration method was used for this analysis. The method is described in Appendix 3. The solids content of the reaction mixture increases due to the methylolation reaction as formaldehyde reacts with melamine to produce methylol melamines.

The condensation and butylation reactions occur simultaneously during the dehydration and acid reaction stages of the process. The methylene ether bridges are produced by the condensation reaction and the butyl ether groups are produced by the butylation reaction. The methylene ether bridges form polymer chains.

Thus, the system for the dehydration and acid reaction stages becomes extremely complex. It was not possible to directly measure quantitatively these chemical species. Therefore, it was very important to devise an indirect method to study this complex system. The method was devised from the following interpretations of the reaction scheme.

The reaction scheme shows that water is produced as a reaction product due to both the condensation and butylation reactions. Therefore the water content of the reaction system as a whole must increase as the reactions proceed. As n-butanol reacts with methylol groups to produce butyl ether groups during the butylation reaction, the n-butanol content of the reaction system must decrease.

It was shown in Section 3.6 that it is possible to measure the solids content of a resin by using the vacuum solids method. This is done by removing all the volatile materials from a resin sample leaving the solids which are actually responsible for the structure of the resin (see Appendix 3). The reaction scheme shows that during the condensation reaction two moles of methylol melamines react with each other releasing a mole of water to produce a mole of methylene ether bridges to link them. A mole of water is thus released to the solvent system from the solids system. Therefore, the solids content must reduced by the molecular weight of water in grams (18 grams) per each mole of methylene ether bridges produced. During the butylation reaction a mole of butanol reacts with a mole of methylol melamines to produce a mole of butyl ether groups and a mole of water. In this case, a mole of n-butanol goes from the solvent system to the solids system, whereas a mole of water is released to the solvent system from the solids system. Therefore, the solids content must increase by 56 grams (74 -18, Mol. wt. of n-butanol - Mol. wt. of water) to produce a mole of butyl ether groups. The overall effect of these two reactions is such that the solids content increases during the process.

The above discussion shows that there are three quantities which change with the reactions. During the dehydration and acid reaction stages, water and solids must increase whereas n-butanol must decrease with the reactions. Two of these, the water produced and the solids content can be measured. The mass balance method was devised to use these measurements to determine the changes in these three quantities during the process, and hence deduce the extent of the chemical reactions at any time. The method is described in Section 5.3. The data produced by this method has been used to quantify the chemical changes occurring during the dehydration and acid reaction stages. This is discussed in Section 5.4.

5.3 THE MASS BALANCE METHOD

The objective of the mass balance method was to collect experimental data regarding the quantitative chemical changes occurring during the process in order to study the process. It is therefore necessary to carry out a mass balance analysis considering all inputs to and outputs from the reactor system. A typical schematic diagram showing all inputs and outputs is given in Figure 5.1. The amounts of sodium hydroxide for pH adjustment and acid catalyst are very small and hence they were ignored in this analysis.

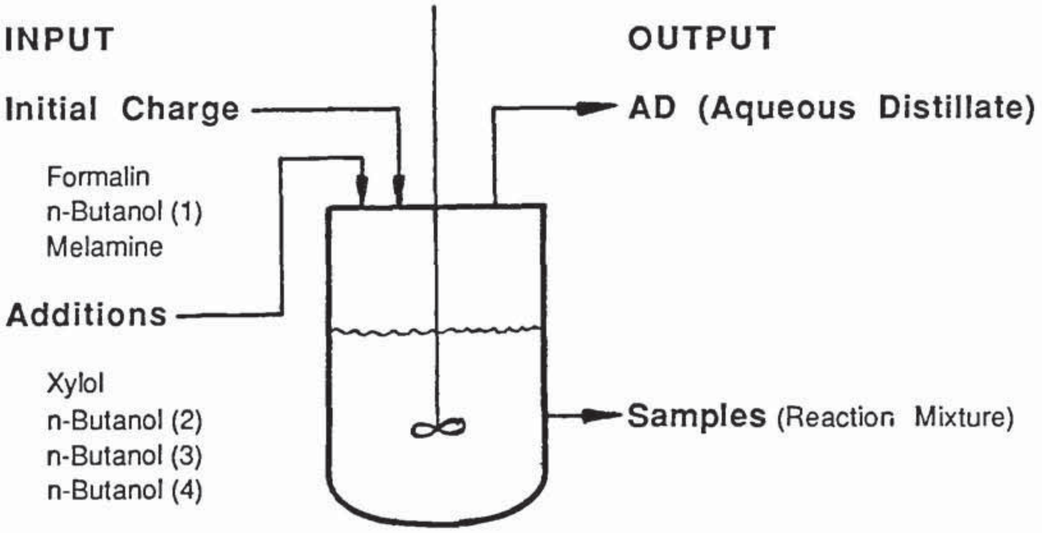


Figure 5.1 A Typical Reactor system with all inputs and outputs

The input side consists of two sources of materials, (a) the initial charge and (b) additions as shown in Figure 5.1. The initial charge consists of formalin, n-butanol (1) and melamine. Xylol is added at the start of the dehydration stage. After 3 hours a second charge of n-butanol is made. Further n-butanol additions are carried out during the acid reaction stage for controlling the viscosity as discussed in Section 3.3.4.

For the experiments, the solvents n-butanol and xylol were charged volumetrically to the reactor. Their quantities were calculated from their densities, which were measured using an Anton Paar DMA 46 digital density meter.

Formalin contains formaldehyde, methanol and water. The analysis of formalin for its compositions was carried out by the control laboratory at BIP. The analytical method used for determining the formaldehyde content of a formalin solution is given in Appendix 3.

The methanol content of a formalin solution was determined from the graph given in Appendix 3, showing the relationship between the methanol content, formaldehyde content and the specific gravity of the formalin solution at 25/25 °C. Specific gravities were determined by using the Anton Paar DMA 46 digital density meter.

Once the formaldehyde and methanol contents of a formalin solution are known, its water content can be calculated by difference. Formalin was charged volumetrically to the reactor. Its weight was calculated from its density. From this quantity, the amounts of formaldehyde, methanol and water can be calculated using their compositions. Thus, it is possible to determine the quantities of all the chemical inputs.

The output from the reactor, shown in Figure 5.1 consists of the aqueous distillate and a series of samples of the reaction mixture, taken at fixed times. A sample of the aqueous distillate consists of all the distillate collected in the interval between two reactor sample times.

A typical arrangement of reaction mixture samples was for one sample at the end of the methylolation stage, four samples at equal intervals, say t_1 minutes, during the dehydration stage, and four samples at equal intervals, say t_2 minutes, during the acid reaction stage. The samples would be designated as shown in Table 5.1.

Table 5.1 Sampling arrangement for the mass balances

Process Stage	Sample No.	Time of each sample from start of stage min	Wt. of Resin Sample g	Wt. of AD removed g	Wt. of reaction mixture in reactor including sample g
Methylolation	1M	End of Methylolation		-	Initial charge
Dehydration	1D	t_1		AD1D	
	2D	$2t_1$		AD2D	
	3D	$3t_1$		AD3D	
	4D	$4t_1$		AD4D	
Acid Reaction	1A	t_2		AD1A	
	2A	$2t_2$		AD2A	
	3A	$3t_2$		AD3A	
	4A	$4t_2$		AD4A	

The third column in Table 5.1, records the time when the samples are taken in each process stage. Thus, during the dehydration stage, the samples 1D to 4D are taken at times t_1, $2t_1$, $3t_1$ and $4t_1$ minutes and similarly, the samples 1A to 4A are taken at times t_2, $2t_2$, $3t_2$ and $4t_2$ minutes in the acid reaction stage.

The fourth column in this Table contains the weights of the reactor samples so that the quantity of reaction mixture taken out of the reactor at a particular time is known.

The fifth column is for recording the weights of the aqueous distillates removed from the reactor system. The weights of the aqueous distillates AD1D to AD4D and AD1A to AD4A are removed during the dehydration and the acid reaction stages respectively. The quantity AD1D is the distillate removed during the time interval 0 to t_1 minutes and similarly the quantity AD2D is removed during the time interval t_1 to $2t_1$ minutes in the dehydration stage.

The last column of this Table is for listing the weight of the material in the reactor at the time of sampling (weight of the reactor sample is included in this quantity). For example, at time t_1 in the dehydration stage, this weight includes the weight of the reactor sample 1D. This weight can be calculated as follows:

Weight of material in the reactor at time t_1 in the dehydration stage

= Wt. of the initial charge - Wt. of the reactor sample 1M + Wt. of xylol - Wt. of the AD, AD1D.

Further n-butanol additions are also included in this analysis at the time they are added.

The whole reactor system can now be expressed in a simple schematic way for the mass balances as shown in Figure 5.2. The components of the whole system are shown in Table 5.2. Solids is the only non-volatile component among all the components shown in Table 5.2.

It is possible to analyse the aqueous distillate using the Gas - Liquid Chromatographic technique. For this work, the AD samples were analysed at the Chemical Engineering Department of the Aston University, using a Gas-Liquid Chromatograph (GLC - Pye Unicam Model 204) with a thermal conductivity detector. A 'Porapak Q' column was used for this analysis. Details of this method is given in Appendix 3. It was concluded from this analysis that xylol does not leave in the aqueous distillates. Thus, the aqueous distillates can be quantitatively analysed for the components shown in Table 5.2.

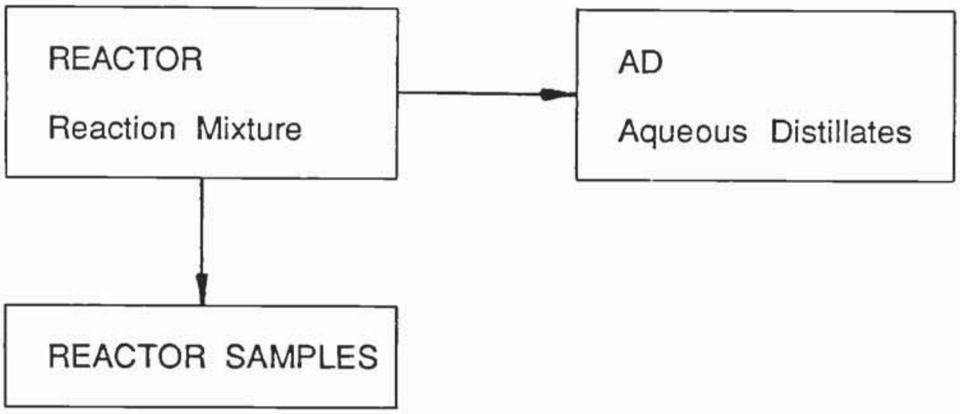


Figure 5.2 Schematic Diagram for the Mass Balances

Table 5.2 Components involved in the whole reactor system

Component	Components present in the Reactor System and Reactor Samples	Components present in the Aqueous Distillate
Water	Yes	Yes
n-Butanol	Yes	Yes
Methanol	Yes	Yes
Xylol	Yes	No
Free Formaldehyde	Yes	Yes
Solids	Yes	No

The methods used for the quantitative analysis of the reactor samples are given in Table 5.3. The first three methods are described in Appendix 3. The quantitative analysis of the solvent n-butanol, methanol and xylol in the resin mixture was not possible as there were no available methods.

Table 5.3 Analytical Methods

Component	Quantitative Method Used
Solids	Vacuum Solids method
Free Formaldehyde	Sulphite (back titration) method
Water	Karl Fischer's Method
Xylol	Mass Balance
Methanol	Mass Balance
n-Butanol	Difference (i.e. 100% - % of the rest)

Xylol and methanol were calculated using mass balances, taking into account the fact that they do not take part in the chemical reactions. Xylol does not leave in the aqueous distillate; however, it does leave in the reactor samples in small quantities which have been considered in this analysis. Similarly the quantity of methanol was calculated allowing for the amounts of methanol in the AD and the reactor samples. The butanol composition (%Wt) of the reaction mixture was calculated by difference. The precautions to be taken during the quantitative analysis are discussed as follows.

The calibrations shown in Appendix 3 for the Gas Liquid Chromatographic method should be checked and updated if required, before the analysis. For the vacuum solids test, the balance must be zeroed every time before weighing a set of sample bottles or empty bottles. For the Karl Fischer's titration method, the Fischer factor for the Fischer reagent must be checked and updated before using the reagent for the analysis.

Once the quantitative analysis of all the components in the whole system is known, it is possible to produce the data regarding the changes in the amounts of water, n-butanol and solids by carrying out component balances.

For example, at the end of the methylolation stage, i.e. the start of the dehydration stage, suppose the water in the reactor was 'A' grams. If after 't_1' minutes in the dehydration stage, the quantities of water in the whole system were as follows:

Table 5.4 Water in the whole reactor system

Sample	Water in the Reactor	Water in AD1D	Water in the previous Sample (1M in this case)
1D	B grams	C grams	D grams

The water produced can be expressed by the following equation:

Water produced in grams $= (B + C + D) - A$

The decrease in the quantity of n-butanol can be calculated in a similar way. Suppose, the n-butanol in the reactor at the start of the dehydration stage was 'E' grams. If, after 't_1' minutes in the dehydration stage, the quantities of n-butanol in the whole system were as follows:

Table 5.5 n-Butanol in the whole reactor system

Sample	n-Butanol in the reactor	n-Butanol in AD1D	n-Butanol in the previous sample (1M in this case)
1D	F grams	G grams	H grams

The n-butanol reacted can be expressed by the following equation:

n-Butanol reacted in grams $= E - (F + G + H)$

Calculations for the increase in the quantity of solids are comparatively easy as only the solids leaving in the reactor samples need to be considered. Suppose, the quantity of solids in the reactor at the start of the dehydration stage was 'I' grams. If, after 't_1' minutes in the dehydration stage, the quantities of solids in the whole system were as follows:

Table 5.6 Solids in the whole reactor system

Sample	Solids in the reactor	Solids in AD1D	Solids in the previous sample (1M in this case)
1D	J grams	-	K grams

The solids produced can be expressed by the following equation:

Solids increased in grams $= (J + K) - I$

Thus, it is possible to deduce the required data from the experimental information using the mass balance method.

5.4 INTERPRETATION OF RESULTS CONSIDERING THE STOICHIOMETRY

The mass balance method discussed above enables the calculation of the amounts of water produced, n-butanol reacted and the solids weight increase in the time between two consecutive samples times. Suppose, the quantities in an interval Δt minutes of the reaction time are:

water produced = W moles,
n-butanol reacted = X moles and
solids increased = S grams.

The following condensation and butylation reactions were considered in Section 5.2 for the dehydration and acid reaction stages:

1. $-\underset{|}{N}.CH_2OH + -\underset{|}{N}.CH_2OH \longrightarrow -\underset{|}{N}.CH_2 - O - CH_2.\underset{|}{N}- + H_2O$

2. $-\underset{|}{N}.CH_2OH + C_4H_9OH \rightleftharpoons -\underset{|}{N}.CH_2.O.C_4H_9 + H_2O$

The data produced by the mass balance method can be interpreted using the stoichiometric relationships of these reactions as follows:

1. Moles of butyl ether groups produced = Moles of n-butanol reacted

   = X

2. Moles of methylene ether bridges produced = Moles of water produced due to the condensation reaction

   = Y

   Now Y = Moles of water produced due to condensation + butylation - Moles of water produced due to butylation

   Thus Y = W - X

3. Moles of methylol groups used up = Moles of methylol groups used up for butylation + condensation

   = Z

   Thus Z = X + 2Y

Thus, it is possible to calculate the changes in the quantities of the required chemical species indirectly from the experimental results. When this analysis is used for the complete reaction time for the dehydration and acid reaction stages, by taking a number of samples, it is possible to produce plots of the variation of these chemical species with the reaction time.

5.5 Calculation of Theoretical Solids for Testing the Analysis

It was shown in the previous section that it is possible to calculate the changes in the extent of the butylation and condensation reactions over a particular reaction time interval (Δt). These calculations are based on the reaction scheme developed in Section 5.2.

The validity of the analysis has been tested by using an additional calculation for the theoretical solids. The formula for the theoretical quantitative increase in solids, using the stoichiometry of the reaction scheme, can be written as follows:

Theoretical Increase in Solids over time Δt

$$= (\text{Mol. wt. of n-butanol} - \text{Mol. wt of water})\,X - (\text{Mol. wt. of water})\,Y$$

$$= (74.12 - 18.015)\,X - 18.015\,Y$$

$$= 56.105\,X - 18.015\,Y \quad \text{grams}$$

It was already seen in the previous section that the experimental quantitative increase in solids over the reaction time Δt is S grams. This can be compared with the theoretical quantitative increase in solids for the same reaction time Δt. If the hypothesis is true then these two quantities must be the same within experimental error as given in equation:

$$\mathbf{S \cong 56.105\ X - 18.015\ Y}$$

5.6 DISCUSSION

The mass balance method was developed to study the chemical changes occurring during the process, because the direct quantitative measurement of the chemical species involved was not possible. It is an indirect method which uses the limited experimental data to calculate data regarding the changes in the quantities of water, n-butanol and solids.

Using this data and the stoichiometry of the theoretical reaction model, the mass balance method predicts the changes in the quantities of the chemical species involved. These predictions have been tested by comparing the changes in the quantity of solids measured and the relevant theoretical solids figure. For the reaction model to be true, these two quantities must be the same within experimental error. This will be tested in Chapter 6.

CHAPTER SIX

COLLECTING KINETIC DATA

6.1 INTRODUCTION

The first set of experimental work was discussed in Chapter 4. This chapter deals with the second set of experimental work. The objective of this work was to collect experimental data regarding the chemical changes occurring during the process and hence to study the chemical reactions involved in the process.

This second set of experimental work consists of a series of laboratory scale and works scale experiments. Table 6.1 contains the summary of the work. The process was studied in stages. The first two experiments VP1 and VP2 were carried out to study the methylolation stage using free formaldehyde analysis to monitor the progress of reaction.

The experiments VP3 and VP4 were performed before the discovery of the mass balance method, described in Chapter 5. A combination of the sulphite method and the iodometric method was used to study the changes in the methylol content during the process. This approach was found unreliable and hence these two experiments have not been discussed in this chapter.

The mass balance method was applied to the rest of the experiments. The experiments VP5 and VP6 were carried out to study the dehydration and acid reaction stages of the process. During the experiments VP7 to VP11, the process was studied by changing the process parameters, n-butanol concentration (VP7 and VP8) and pH (VP9, 10 and 11). The works process was also studied using the mass balance method and is compared with the laboratory process.

Table 6.1 Summary of the experiments

Experiment No.	Process Stage studied/ Process condition	Method used for the analysis
VP1	Methylolation / Extended	Sulphite (Back titration)
VP2	Methylolation / Extended	Sulphite (Back titration)
VP3	Dehydration	Sulphite + Iodometric
VP4	Dehydration	Sulphite + Iodometric
VP5	Dehydration & Acid Reaction	Mass Balance
VP6	Dehydration & Acid Reaction	Mass Balance
VP7	Dehydration / Increased butanol	Mass Balance
VP8	Dehydration / Decreased butanol	Mass Balance
VP9	Dehydration / High pH	Mass Balance
VP10	Dehydration / Low pH	Mass Balance
VP11	Dehydration / Normal pH (Extended Dehydration)	Mass Balance
Works 1	Dehydration & Acid Reaction	Mass Balance
Works 2	Dehydration & Acid Reaction	Mass Balance

6.2 METHYLOLATION STAGE

Methylolation is the process stage from the beginning of heat application to the completion of the 15 minutes total reflux period. The stage was discribed in Section 3.3.2.

Two laboratory experiments VP1 and VP2 were carried out to study the methylolation reaction. The works procedure was followed exactly up to the end of 15 minutes total reflux period. Additionally during these experiments, the total reflux period was extended for further thirty minutes. Samples were taken at intervals of ten minutes. The sample bottles were quenched into a bath of dry ice and acetone immediately after sampling and then were stored in a refridgerator to prevent the methylolation reaction occurring in the sample.

Reaction temperature was monitored throughout the process. During these experiments boiling commenced at the 25th minute. Details of these experiments are given in Appendix 4. During the experiment VP1, the molar ratio of formaldehyde to melamine was slightly higher than that used for the plant production, 5.47 instead of 5.25. This error was corrected during the experiment VP2 and the results of this experiment are discussed in this section. The temperature versus reaction time plot is given in Figure 6.1.

The samples were analysed for their free formaldehyde contents, using the sulphite (back titration) method. From this analysis, data of free formaldehyde concentration (mole / litre) as a function of reaction time was produced. Details of this analysis are included in Appendix 4. The free formaldehyde concentration versus the reaction time plot is given in Figure 6.2.

6.2.1 Discussion and Conclusions

Figure 6.2 shows that the change in free formaldehyde concentration was very small during the first 10 minutes of the reaction time. During this period the reaction temperature rose from 28 °C to 43 °C. The reaction rates were low because of this low temperature.

The free formaldehyde concentration changed greatly between 10 and 30 minutes of the reaction time. The formaldehyde reacted during this period to form methylol melamines. The reaction temperature rose from 43 °C to 93 °C during this period.

Further changes in free formaldehyde concentration were very small or negligible after 30 minutes. The standard methylolation stage lasts for 40 minutes, i.e. 15 minutes after commencement of boiling. For these experiments this

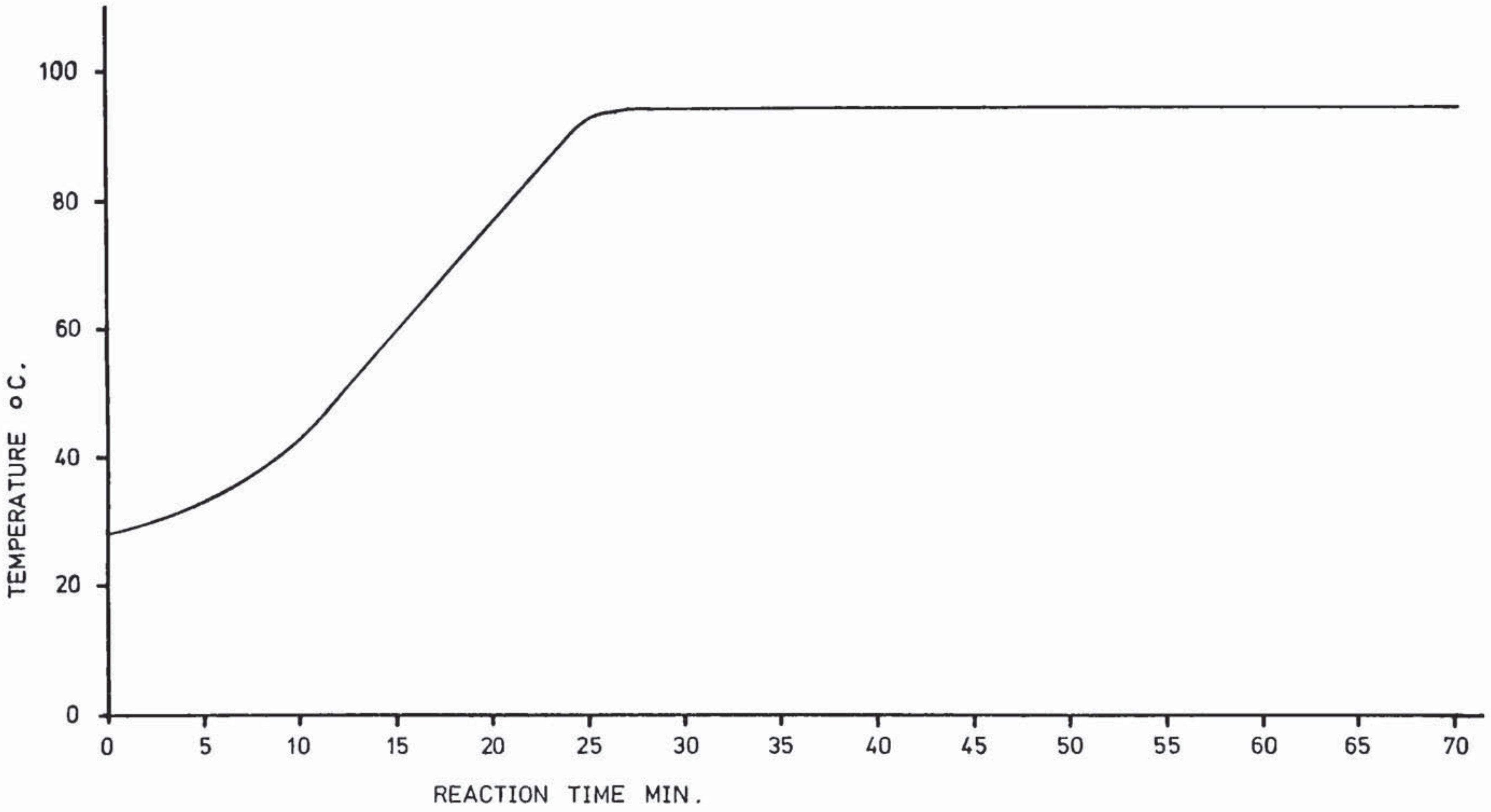
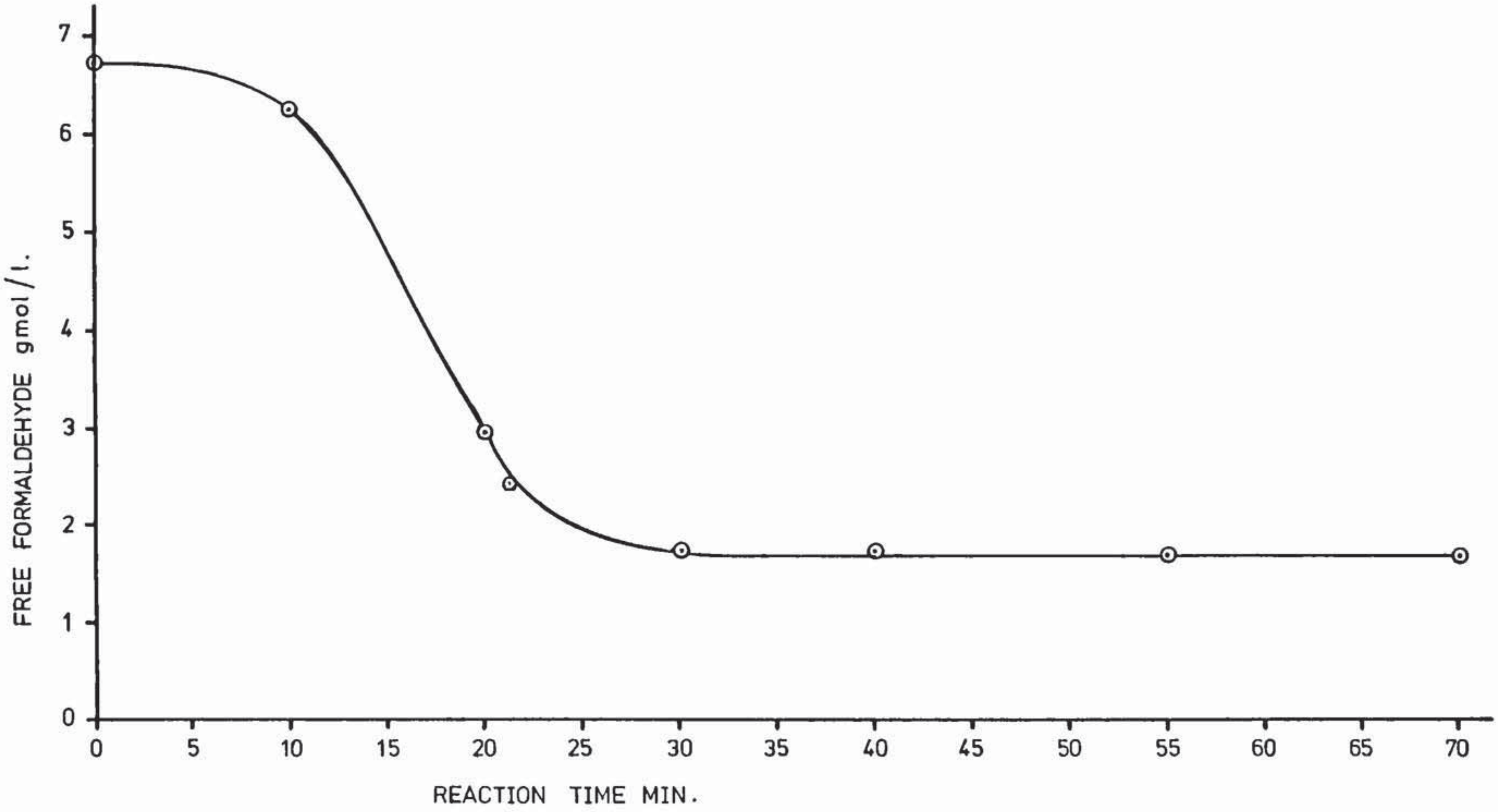


Figure 6.1 Temperature / Reaction Time Plot for the Experiment VP2



<u>Figure 6.2</u> Free Formaldehyde / Reaction Time Plot for the Experiment VP2

stage was extended for a further 30 minutes, to ensure completion of reaction. In Section 2.3.1 it was shown that the addition reaction is an equilibrium reaction. Figure 6.2 shows that the equilibrium state was reached after 25 minutes of the reaction time.

The degree of addition or methylolation was found to be four as follows:

$$\text{Degree of addition} = \frac{\text{moles of formaldehyde reacted}}{\text{moles of melamine}}$$

$$= \frac{(\text{Initial formaldehyde - formaldehyde at the end of the stage})/\text{Mol. Wt.}}{\text{Moles of melamine}}$$

$$= \frac{(856.54 - 213.10)/(30.03)}{5.39} = \frac{21.43}{5.39}$$

$$= 3.98 \cong 4$$

That means four methylols ($-CH_2OH$) were formed per melamine molecule.

The degree of addition found was based on the free formaldehyde analysis only (experiments VP1 and VP2). The vacuum solids analysis of the experiments VP5-VP11 confirmed the degree of addition during the methylolation stage to be around four. This is discussed in further sections of this chapter. The results are summarized in Table 6.2.

During the experiment VP11, a sample of the reaction mixtutre was taken after 22 minutes of the methylolation stage. This sample was analysed for its solids and free formaldehyde content. The quantities of formaldehyde reacted and the solids increase were found to be nearly the same, 573.23 g and 573.43 g respectively. This shows that the weight increase was due to addition of formaldehyde. The result of the free formaldehyde analysis has been included in Figure 6.2.

Table 6.2 Degree of addition based on solids content of reactor samples

Experiment No.	Formaldehyde Reacted g	Solids Increased g	Methylols produced mol.	Degree of Addition
VP5	630.61	631.08	21.01	3.90
VP6	641.45	639.92	21.31	3.95
VP7	646.63	649.88	21.64	4.02
VP8	643.55	643.63	21.43	3.98
VP9	645.32	645.51	21.49	3.99
VP10	646.55	646.55	21.53	3.99
VP11	645.62	645.62	21.50	3.99

6.3 DEHYDRATION AND ACID REACTION STAGES

The dehydration and acid reaction stages were described in Sections 3.3.3 and 3.3.4 respectively. Two laboratory experiments VP5 and VP6 were carried out to study the chemical changes occurring during these stages.

The molar ratios of raw materials were kept exactly the same as that of a works batch (Formaldehyde : Melamine : n-Butanol = 5.25 : 1 : 3.74). The mass balance method described in Chapter 5 was applied to collect the experimental data regarding the chemical changes. The experiment VP5 is discussed in detail to illustrate the use of the mass balance method as follows.

6.3.1 Experiment VP5

Details about the raw materials used for this experiment are given in Appendix 4. Compositions of the initial charge were known and are listed in Table 6.3. Samples of the resin mixtures and aqueous distillates (AD) were collected during the process. The sample bottles for the resin mixtures were immediately quenched into cold water after sampling and were then stored in a refridgerator to prevent the chemical reactions going ahead. The resin samples were weighed to include the total sample weight in the mass balance. More detail about the experiment is given in Appendix 4. Table 6.4 shows when the samples were taken during the process. It also includes the amount of AD removed during the periods between two consecutive sampling times.

The resin samples and AD samples were analysed using the methods described in Chapter 5. The results of this analytical work are listed in Tables 6.5, 6.6 and 6.7. Table 6.5 contains the analysis of the resin samples from the reactor. Total quantity of the resin product listed in this table for any time also includes the weight of the resin sample taken at that time. Table 6.6 contains the analysis of the aqueous distillates removed from the reactor whereas Table 6.7 contains the information about the materials taken out with the resin samples.

Mass balances for water, n-butanol and solids were produced from this data. The objective of the mass balance calculations was to determine the quantities of water was produced, the n-butanol reacted and the increase in solids during a particular time interval, which is the difference between two consecutive sampling times. The mass balances for water, n-butanol and solids are given in Tables 6.8, 6.9 and 6.10 respectively.

The above discussions illustrate the use of the mass balance method to collect experimental data regarding the changes in the quantities of water, n-butanol and solids. The results have been summerized in Table 6.11.

Table 6.3 Initial Charge : Experiment VP5

Material	Quantity g	Composition % (wt)
Melamine	680.00	16.51
n-Butanol	1493.40	36.26
Formaldehyde	851.01	20.66
Water	1024.60	20.87
Methanol	70.04	1.70
Total	4119.00	100.00

Table 6.4 Sampling Details : Experiment VP5

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	1M	40 End of Methylolation	19.1	4119.0	-
Dehydration	1D	80	24.8	3953.0	374.1
	2D	160	27.0	3445.0	483.0
	3D	240	26.0	3463.4	325.7
Acid Reaction	1A	60	25.0	3535.3	144.1
	2A	120	24.0	3416.8	93.5
	3A	180	25.0	3363.8	29.0
	4A	230	24.2	3364.1	15.0

Table 6.5 Materials in the reactor : Experiment VP5

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.87	36.26	1.70	-	20.66	16.51	
		g	1024.60	1493.40	70.04		851.01	680.00	4119.0
1M	40	%	24.87	36.26	1.70	-	5.35	31.83	
		g	1024.60	1493.40	70.04		220.40	1311.08	4119.0
1D	80	%	22.85	21.85	1.12	5.75	5.00	43.43	
		g	903.26	863.73	44.28	227.10	197.65	1716.79	3953.0
2D	160	%	14.17	23.95	0.65	6.55	4.93	49.75	
		g	488.16	825.08	22.26	225.67	169.84	1713.89	3445.0
3D	240	%	5.85	33.76	0.40	6.46	4.33	49.20	
		g	202.61	1169.24	13.94	223.90	149.97	1703.99	3463.0
1A	60	%	3.70	34.89	0.29	6.29	3.97	50.86	
		g	130.81	1233.47	10.24	222.22	140.35	1798.05	3535.3
2A	120	%	2.50	32.10	0.23	6.46	3.91	54.80	
		g	85.42	1096.79	7.83	220.65	133.60	1872.41	3416.8
3A	180	%	1.90	31.99	0.21	6.51	3.89	55.50	
		g	63.91	1076.08	7.04	219.10	130.85	1866.91	3363.8
4A	230	%	1.55	32.76	0.20	6.46	3.83	55.20	
		g	52.14	1102.08	6.61	217.47	128.85	1856.98	3364.1

Table 6.6 Materials in AD : Experiment VP5

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	80	%	83.20	4.50	6.80	-	5.50	-	
		g	311.25	16.84	25.44		20.58		374.1
2D	160	%	85.30	4.70	4.50	-	5.50	-	
		g	412.00	22.70	21.74		26.56		483.0
3D	240	%	86.90	4.90	2.50	-	5.70	-	
		g	283.03	15.96	8.14		18.56		325.7
1A	60	%	86.60	5.00	2.50	-	5.90	-	
		g	124.79	7.20	3.60		8.50		144.1
2A	120	%	82.40	9.00	2.50	-	6.10	-	
		g	77.04	8.41	2.34		5.70		93.5
3A	180	%	81.50	9.70	2.50	-	6.30	-	
		g	23.63	2.81	0.73		1.83		29.0
4A	230	%	81.50	9.70	2.50	-	6.30	-	
		g	12.22	1.46	0.38		0.95		15.0

Table 6.7 Materials in Samples : Experiment VP5

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	40	g	4.75	6.93	0.32	-	1.02	6.08	19.1
1D	80	g	5.67	5.42	0.28	1.43	1.24	10.77	24.8
2D	160	g	3.83	6.47	0.18	1.77	1.33	13.43	27.0
3D	240	g	1.52	8.78	0.10	1.68	1.13	12.79	26.0
1A	60	g	0.93	8.72	0.07	1.57	0.99	12.72	25.0
2A	120	g	0.60	7.70	0.06	1.55	0.94	13.15	24.0
3A	180	g	0.48	8.00	0.05	1.63	0.97	13.88	25.0

Table 6.8 Mass Balance for Water : Experiment VP5

Sample No.	Time in Process Stage min	Water in the reactor g	Water off with AD g	Water off with sample g	Total g	Water Produced g	gmol
1M	40	1024.60					
1D	80	903.26	311.25	4.75	1219.26	194.66	10.81
2D	160	488.16	412.00	5.67	905.83	2.57	0.14
3D	240	202.61	283.03	3.83	489.47	1.31	0.07
1A	60	130.81	124.79	1.52	257.12	54.51	3.03
2A	120	85.42	77.04	0.93	163.39	32.58	1.81
3A	180	63.91	23.63	0.60	88.14	2.72	0.15
4A	230	52.14	12.22	0.48	64.84	0.93	0.05

Table 6.9 Mass Balance for n-Butanol : Experiment VP5

Sample No.	Time in Process Stage min	Butanol in the reactor g	Butanol off with AD g	Butanol off with sample g	Total g	Butanol Reacted g	gmol
1M	40	1493.40					
1D	80	863.73	16.84	6.93	887.50	605.90	8.17
2D	160	825.08 (+370.32)	22.70	5.42	853.20	10.53	0.14
3D	240	1169.24 (+242.04)	15.96	6.47	1191.67	3.73	0.05
1A	60	1233.47	7.20	8.78	1249.45	161.83	2.18
2A	120	1096.79	8.41	8.72	1113.92	119.55	1.61
3A	180	1076.08 (+40.34)	2.81	7.70	1086.59	10.20	0.14
4A	230	1102.08	1.46	8.00	1111.54	4.88	0.06

Table 6.10 Mass Balance for Solids : Experiment VP5

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
1M	40	1311.08	-	-	1311.08	631.08
1D	80	1716.79	-	6.08	1722.87	411.79
2D	160	1713.89	-	10.77	1724.66	7.87
3D	240	1703.99	-	13.43	1717.42	3.53
1A	60	1798.05	-	12.79	1810.84	106.85
2A	120	1872.41	-	12.72	1885.13	87.08
3A	180	1866.91	-	13.15	1880.06	7.65
4A	230	1856.98	-	13.88	1870.86	3.95

Table 6.11 Results of the mass balances for Experiment VP5

Process Stage	Sample No.	Differential Time Δt min	Water Produced g	Water Produced gmol	n-Butanol Reacted g	n-Butanol Reacted gmol	Solids Increase g
Methylolation	1M	40	-	-	-	-	631.08
Dehydration	1D	80	194.66	10.81	605.90	8.17	411.79
	2D	80	2.57	0.14	10.53	0.14	7.87
	3D	80	1.31	0.07	3.73	0.05	3.53
Acid Reaction	1A	60	54.51	3.03	161.83	2.18	106.85
	2A	60	32.58	1.81	119.55	1.61	87.08
	3A	60	2.72	0.15	10.20	0.14	7.65
	4A	50	0.93	0.05	4.88	0.06	3.95

6.3.2 Experiment VP6

The molar ratio of raw materials were kept exactly the same as that of the experiment VP5. The experimental procedure was kept exactly the same as before, except for the fact that two additional samples were taken during this experiment and 50 ml more butanol was added to the reactor during the acid reaction satge. Table 6.12 shows when the samples were taken during the process.

Details about the raw materials, compositions of the initial charge, the experiment, the analytical work and the mass balances are given in Appendix 4 as follows:

Table A4.5	Raw Materials : VP6
Table A4.6	Initial Charge : VP6
Table A4.7	Experimental detail : VP6
Table A4.8	Materials in the reactor : VP6
Table A4.9	Materials in AD : VP6
Table A4.10	Materials in samples : VP6
Table A4.11	Mass balance for water : VP6
Table A4.12	Mass balance for n-butanol :VP6
Table A4.13	Mass balance for solids : VP6

Only the final results produced by the mass balance method have been considered in the main text and are given in Table 6.13.

Table 6.13 does not contain the results for the sample 2D. This was because the results produced from the analysis of the sample 2D were not consistent with the rest of the analysis. It was concluded from an investigation that the sample 2D was not a representative sample of the reaction mixture. This can be explained as follows.

The sample 2D was taken at the 80th minute of the dehydration stage. The water content of the resin mixture was high at this time. As a result of this, when the stirrer was stopped to pipette out a sample from the reactor, the aqueous phase present in the reactor separated out from the solvent phase. Therefore, the sample was not representative of the resin mixture. In subsequent experiments care was taken to remove the sample before separation of the phases could occur and no further problem was experienced.

Table 6.12 Sampling Details : Experiment VP6

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	1M	40 End of Methylolation	23.7	4118.31	-
Dehydration	1D	40	22.6	4063.76	258.07
	2D	80	20.6	3834.96	206.20
	3D	160	22.8	3467.22	347.14
	4D	240	18.4	3417.64	396.64
Acid Reaction	1A	40	19.3	3302.91	96.33
	2A	80	20.2	3451.82	73.53
	3A	120	19.8	3385.83	45.79
	4A	180	20.3	3408.70	37.91
	5A	240	21.9	3369.45	18.95

Table 6.13 Results of the mass balances for Experiment VP6

Process Stage	Sample No.	Differential Time Δt min	Water Produced		n-Butanol Reacted		Solids Increase
			g	gmol	g	gmol	g
Methylolation	1M	40	-	-	-	-	639.92
Dehydration	1D	40	187.13	10.39	586.64	7.91	398.52
	3D	120	21.44	1.19	61.20	0.83	39.64
	4D	80	3.28	0.18	12.71	0.17	8.84
Acid Reaction	1A	40	34.60	1.92	102 81	1.39	68.18
	2A	40	27.74	1.54	77.95	1.05	49.99
	3A	40	19.17	1.06	52.63	0.71	31.62
	4A	60	2.69	0.15	10.73	0.14	7.96
	5A	60	0.84	0.15	2.19	0.03	1.53

6.3.3 Interpretation of the Results

Table 6.11 and Table 6.13 contain the experimental data produced by the mass balance method for the experiments VP5 and VP6 respectively. During these experiments, the objective was to study the chemical changes occurring during the dehydration and acid reaction stages. However, it was also possible to calculate the extent of the reaction at the end of the methylolation stage from a sample taken at the end of this stage (1M) for each experiment.

(a) Methylolation Stage

The samples taken at the end of this stage were analysed for solid and free formaldehyde content. These samples were not analysed for water contents by the Karl Fischer's titrations since they were not sufficiently soluble.

The water and n-butanol contents of these samples were taken as constant since the condensation and butylation reactions were not thought to occur during the methylolation stage. However, if the compositions listed in Table 6.4 for the sample 1M (experiment VP5) are added up, the total becomes 100.01% as follows:

Water	24.87	% Wt	(Same as initial)
n-butanol	36.26	% Wt	(Same as initial)
Methanol	1.70	% Wt	(Same as initial)
Free Formaldehyde	5.35	% Wt	(Measured)
Solids	31.83	% Wt	(Measured)
Total	100.01		

The above analysis confirms that the water and n-butanol contents remained constant and no condensation and butylation reactions have occurred. Similarly, the results of the experiment VP6 have supported this conclusion.

The quantity in moles of methylols ($-CH_2OH$) produced as a result of the methylolation reaction is equivalent to the quantity in moles of formaldehyde reacted. The quantity of reacted formaldehyde can be obtained by measuring the decrease in free formaldehyde content or the increase in solids content of the resin solution. This was shown in Section 6.2.

The amount of methylol produced and the degree of additon or methylolation were calculated using the following formulae:

$$\text{Moles of methylol produced} = \frac{\text{Solids increase in grams}}{\text{Mol. Wt. of formaldehyde}} \quad (30.03)$$

$$\text{Degree of addition} = \frac{\text{Moles of Methylols produced}}{\text{Moles of melamine used}} \quad (5.39)$$

The results are listed in Table 6.14.

Table 6.14 Degree of addition : Experiments VP5 and VP6

Experiment No.	Solids increase g	Methylols Produced gmol	Degree of Addition
VP5	631.08	21.03	3.90
VP6	639.92	21.31	3.95

(b) Dehydration and Acid Reaction Stages

The following formulae were derived in Chapter 5, Section 5.3.

If,

water produced = W moles,
n-butanol reacted = X moles and
solids increased = S grams

per Δt minutes of the reaction time, then:

1. Moles of butyl ether groups produced = X
2. Moles of methylene ether bridges produced, Y = W - X
3. Moles of methylol groups reacted, Z = X + 2Y
4. Theoretical increase in solids = 56.105 X - 18.015Y grams

The quantities X, Y and Z were calculated from the results listed in Tables 6.11 and 6.13 and are reported in Table 6.15 and Table 6.16 for the experiments VP5 and VP6 respectively. From these results the theoretical increase in solids were calculated and are reported in Table 6.17 and Table 6.18 for the experiments VP5 and VP6 respectively. These tables also contain the data regarding the practical increase in solids, so that the respective practical and theoretical solids can be compared.

Table 6.19 and Table 6.20 contain the data regarding the quantities; methylene ether bridges, butyl ether groups and methylols as a function of reaction time for the experiments VP5 and VP6 respectively. From this data the plots of butyl ether, methylene ether and methylols versus the reaction time were produced and are given in Figures 6.3, 6.4 and 6.5 respectively.

Table 6.15 Chemical changes over a differential reaction time for VP5

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Dehydration	1D	80	8.17	2.64	13.45
	2D	80	0.14	0.00	0.14
	3D	80	0.05	0.02	0.09
Acid Reaction	1A	60	2.18	0.85	3.88
	2A	60	1.61	0.20	2.01
	3A	60	0.14	0.01	0.16
	4A	50	0.06	0.00	0.06

Table 6.16 Chemical changes over a differential reaction time for VP6

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Dehydration	1D	40	7.91	2.48	12.87
	3D	120	0.83	0.36	1.55
	4D	80	0.17	0.01	0.19
Acid Reaction	1A	40	1.39	0.53	2.45
	2A	40	1.05	0.49	2.03
	3A	40	0.71	0.35	1.41
	4A	60	0.14	0.01	0.16
	5A	60	0.03	0.02	0.07

Table 6.17 Experimental and Theoretical Solids for VP5

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Dehydration	1D	80	411.79	410.82
	2D	80	7.87	7.85
	3D	80	3.53	2.44
Acid Reaction	1A	60	106.85	107.00
	2A	60	87.08	86.73
	3A	60	7.65	7.67
	4A	50	3.95	3.37

Table 6.18 Experimental and Theoretical Solids for VP6

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Dehydration	1D	40	398.52	399.11
	3D	120	39.64	40.08
	4D	80	8.84	9.36
Acid Reaction	1A	40	68.18	68.44
	2A	40	49.99	50.08
	3A	40	31.62	33.53
	4A	60	7.96	7.67
	5A	60	1.53	1.32

Table 6.19 Chemical changes as a function of time for VP5

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
End of Methylolation	1M	40	-	-	21.02
Dehydration	1D	80	2.64	8.17	7.57
	2D	160	2.64	8.31	7.43
	3D	240	2.66	8.36	7.34
Acid Reaction	1A	60	3.51	10.54	3.46
	2A	120	3.71	12.15	1.45
	3A	180	3.72	12.29	1.29
	4A	230	3.72	12.35	1.23

Table 6.20 Chemical changes as a function of time for VP6

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
End of Methylolation	1M	40	-	-	21.31
Dehydration	1D	40	2.48	7.91	8.44
	3D	160	2.84	8.74	6.89
	4D	240	2.85	8.91	6.70
Acid Reaction	1A	40	3.38	10.30	4.25
	2A	80	3.87	11.35	2.22
	3A	120	4.22	12.06	0.81
	4A	180	4.23	12.20	0.65
	5A	240	4.25	12.23	0.58

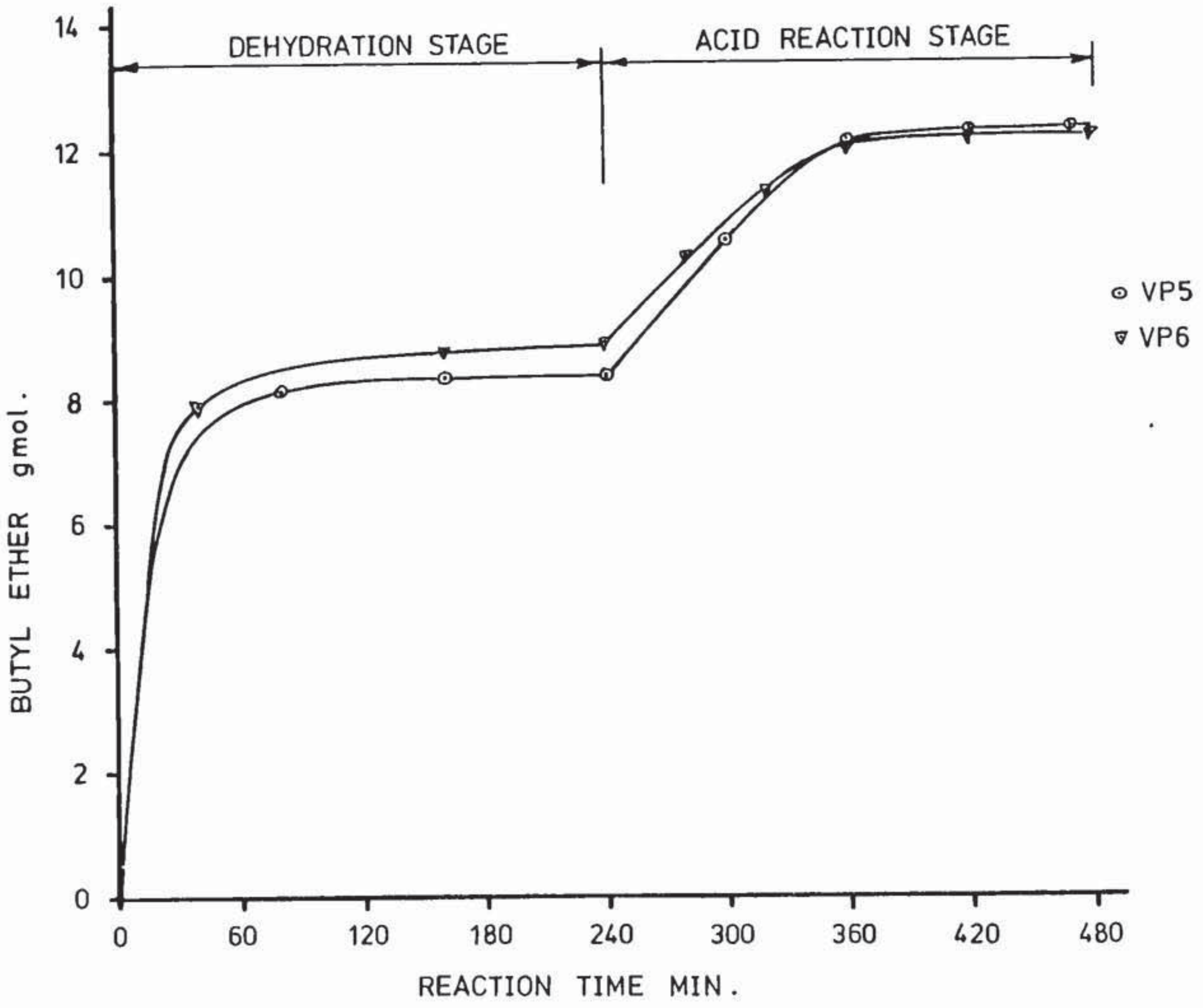


Figure 6.3 Butyl Ether / Reaction Time Plots for the Experiments VP5 and VP6

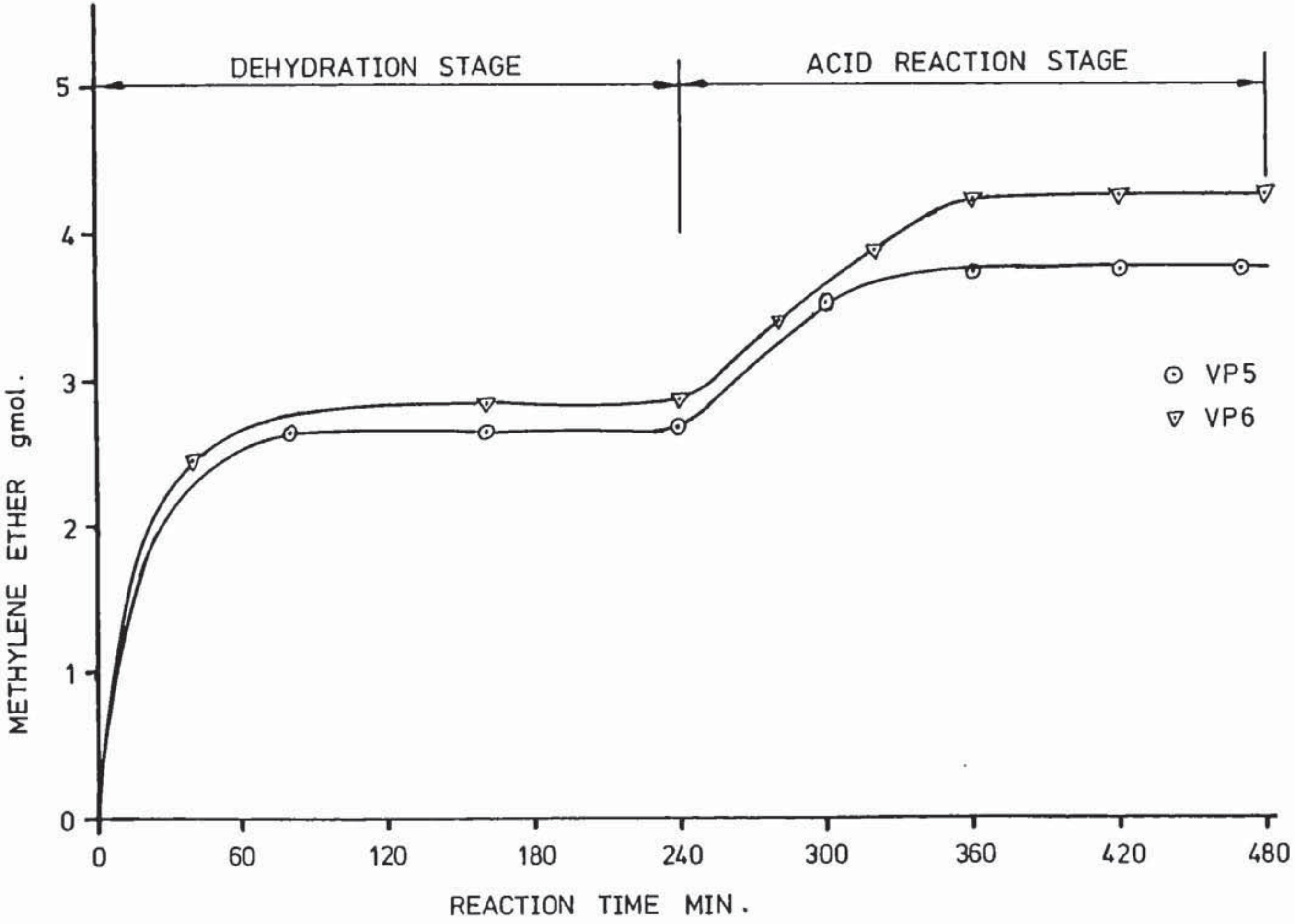


Figure 6.4 Methylene Ether / Reaction Time Plots for the Experiments VP5 and VP6

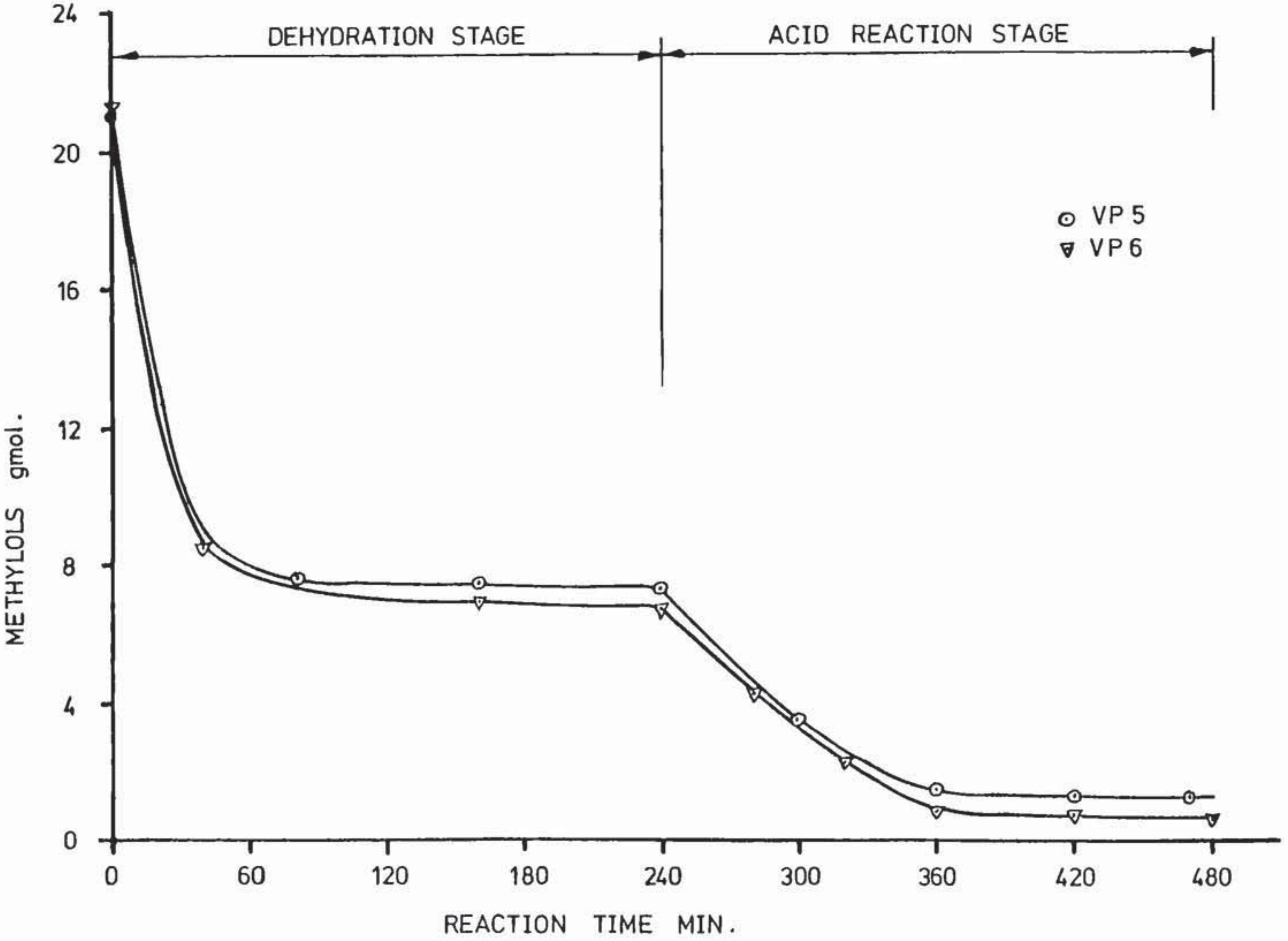


Figure 6.5 Methylols / Reaction Time Plots for the Experiments VP5 and VP6

6.3.4 Discussion and Conclusions

The experimental results have shown that the mass balance method can be used reliably to obtain data regarding the chemical changes occurring during the process. This has been confirmed by comparison of the theoretical and experimental quantities of solids within the experimental errors. For the mass balance analysis, a reaction mixture sample must be a representative sample of the reaction system while sampling from the reactor or while taking it out of a sample bottle for analysis. The experimental results have improved the understanding of the chemical reactions occurring during the process. The following conclusions are drawn from these results:

1. **Methylolation Stage**

(i) The degree of addition is 4. This means on average, four methylols are produced on each melamine molecule.

(ii) The condensation and butylation reactions do not significantly occur during the methylolation stage.

2. **Dehydration and Acid Reaction Stages**

(i) The condensation and butylation reactions as shown in Section 5.2 occur simultaneously during these stages.

(ii) The chemical reactions mainly occur during the first 80 minutes of the dehydration stage and the first 120 minutes of the acid reaction stage. The chemical changes occurring during the remaining periods are very small. Water removal from the reactor is the main activity during these periods.

(iii) At the end of the dehydration stage 2.76 gmoles of methylene ether bridges and 8.63 gmoles of butyl ether groups (average data from VP5 and VP6) have been produced. During the acid reaction stage these quantities are increased by 1.23 gmoles and 3.66 gmoles respectively. Thus, at the end of the process, the quantities of methylene ether and butyl ether produced are 3.99 gmoles and

12.29 gmoles respectively. The amount of melamine used for each of these experiments was 5.39 gmoles. Therefore, on average, 0.74 gmoles of methylene ether and 2.28 gmoles of butyl ether are produced per gmole of melamine.

6.4 EFFECT OF n-BUTANOL CONCENTRATION ON THE DEHYDRATION STAGE

Two experiments VP7 and VP8 were carried out to investigate the effect of changes in the quantity of n-butanol (1) on the chemical reactions. The acid reaction stage was excluded from the process during these experiments. The objective was to study the effect on the chemical reactions during the dehydration stage.

The quantity of n-butanol (1) was increased by 15% (vol) more than the standard charge in experiment VP7. The molar ratios of raw materials thus became; formaldehyde: melamine: n-butanol = 5.31 : 1: 4.30.

The quantity of n-butanol (1) was decreased by 10% (vol) less than the standard charge in experiment VP8. In this case the molar ratios of raw materials became; formaldehyde : melamine : n-butanol = 5.30 : 1 : 3.36.

Five resin samples were taken during each of these experiments. Tables 6.20 and 6.21 contain the information regarding sampling during the process. Details about the raw materials, the experiments, the analytical work and the mass balances are given in Appendix 4 for the experiments VP7 and VP8.

The results produced by the mass balance method are considered here and are given in Tables 6.23 and 6.24 for the experiments VP7 and VP8 respectively. Useful information regarding the chemical changes was obtained from these results and is reported as follows:

Table 6.25	Chemical changes over a differential reaction time for VP7
Table 6.26	Chemical changes over a differential reaction time for VP8
Table 6.27	Experimental and theoretical solids for VP7
Table 6.28	Experimental and theoretical solids for VP8
Table 6.29	Chemical changes as a function of time for VP7
Table 6.30	Chemical changes as a function of time for VP8

The plots of butyl ether, methylene ether and methylols versus reaction time were produced from this data for both the experiments and are given in Figures 6.6, 6.7 and 6.8 respectively.

Table 6.21 Sampling Details : Experiment VP7

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	1M	40 End of Methylolation	15.9	4343.18	-
Dehydration	1D	40	15.9	4342.55	212.01
	2D	80	18.7	4108.74	217.91
	3D	160	23.6	3560.87	529.17
	4D	215	31.9	3649.44	257.69

Table 6.22 Sampling Details : Experiment VP8

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	1M	40 End of Methylolation	17.9	3970.09	-
Dehydration	1D	40	23.5	3994.80	184.75
	2D	80	23.5	3784.28	187.02
	3D	160	23.2	3272.16	488.62
	4D	240	29.2	3267.62	351.20

Table 6.23 Results of the mass balances for VP7

Process Stage	Sample No.	Differential Time Δt min	Water Produced g	Water Produced gmol	n-Butanol Reacted g	n-Butanol Reacted gmol	Solids Increase g
Methylolation	1M	40	-	-	-	-	649.88
Dehydration	1D	40	147.32	8.18	518.12	6.99	367.77
	2D	40	55.31	3.07	123.42	1.67	67.73
	3D	80	13.66	0.76	52.04	0.70	40.27
	4D	55	1.53	0.08	5.03	0.07	4.11

Table 6.24 Results of the mass balances for VP8

Process Stage	Sample No.	Differential Time Δt min	Water Produced g	Water Produced gmol	n-Butanol Reacted g	n-Butanol Reacted gmol	Solids Increase g
Methylolation	1M	40	-	-	-	-	643.63
Dehydration	1D	40	142.04	7.88	529.01	7.14	386.52
	2D	40	47.63	2.64	83.71	1.13	35.27
	3D	80	17.28	0.96	43.11	0.58	25.38
	4D	80	1.05	0.06	2.88	0.04	1.46

Table 6.25 Chemical changes over a differential reaction time for VP7

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Dehydration	1D	40	6.99	1.19	9.37
	2D	40	1.67	1.40	4.47
	3D	80	0.70	0.06	0.82
	4D	55	0.07	0.01	0.09

Table 6.26 Chemical changes over a differential reaction time for VP8

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Dehydration	1D	40	7.14	0.74	8.62
	2D	40	1.13	1.51	4.15
	3D	80	0.58	0.38	1.34
	4D	80	0.04	0.02	0.08

Table 6.27 Experimental and theoretical solids for VP7

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Dehydration	1D	40	367.77	368.49
	2D	40	67.73	68.47
	3D	80	40.27	38.19
	4D	55	4.11	3.75

Table 6.28 Experimental and theoretical solids for VP8

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Dehydration	1D	40	386.52	387.26
	2D	40	35.27	36.20
	3D	80	25.38	25.70
	4D	80	1.46	1.88

Table 6.29 Chemical changes as a function of time for VP7

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
End of Methylolation	1M	40	-	-	21.64
Dehydration	1D	40	1.19	6.99	12.27
	2D	80	2.59	8.66	7.80
	3D	160	2.65	9.36	6.98
	4D	215	2.66	9.43	6.89

Table 6.30 Chemical changes as a function of time for VP8

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
End of Methylolation	1M	40	-	-	21.43
Dehydration	1D	40	0.74	7.14	12.81
	2D	80	2.25	8.27	8.66
	3D	160	2.63	8.85	7.32
	4D	240	2.65	8.89	7.24

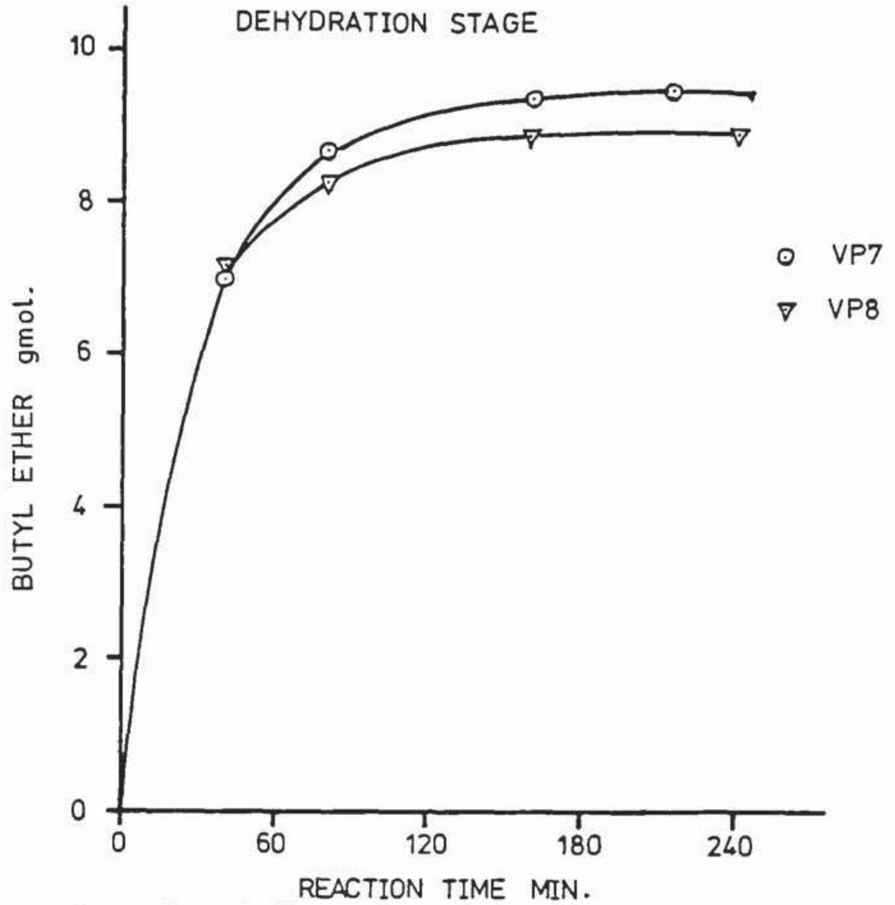


Figure 6.6 Butyl Ether/Reaction Plots for Experiments VP7 and VP8

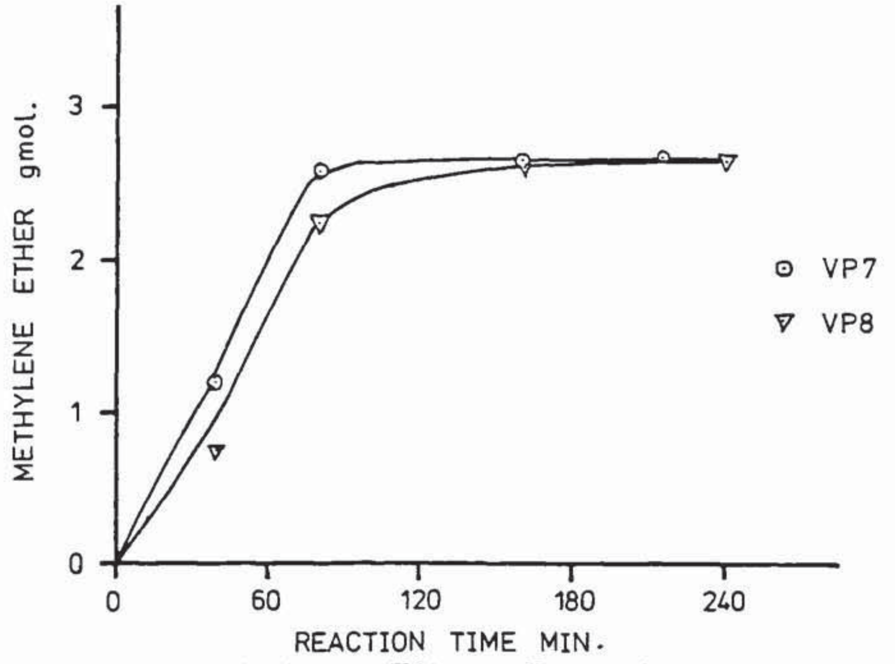


Figure 6.7 Methylene Ether/Reaction Plots for the Experiments VP7 and VP8

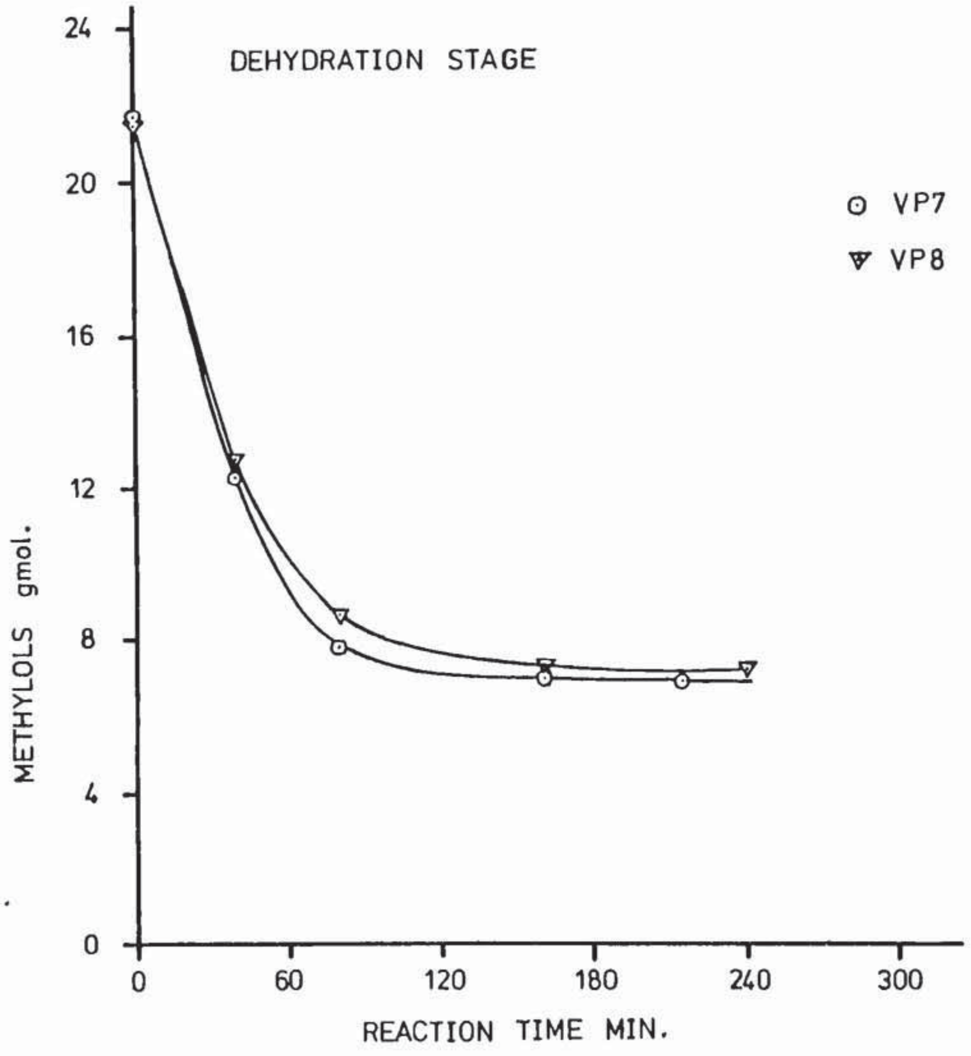


Figure 6.8 Methylols / Reaction Time Plots for the Experiments VP7 and VP8

6.4.1 Discussion and Conclusions

The two experiments, VP7 and VP8 were carried out to investigate the effects of deviations in the quantity of n-butanol (1), were not the ideal experiments as the process conditions excluding the butanol concentration used in them were not exactly the same. These two experiments were performed using different formalin solutions. They were performed on different days using different 44% (wt) formalin solution. The pH adjustment stages were different in these two experiments. Thus, the quality of the resins produced was affected not only by the n-butanol concentrations but also by the changes in the other process conditions.

Figures 6.6 and 6.7 show that there is no significant difference in the quality of the resins produced from these two batches. The resin from the experiment VP7 was found to be slightly more butylated than that from the experiment VP8. The deviations made in the butanol concentration were not large enough to cause considerable effect on the quality of the resins. The experimental results confirmed the conclusions drawn in Section 6.3.4 for the experiments VP5 and VP6.

6.5 EFFECT OF pH

Three experiments VP9, VP10 and VP11 were carried out to investigate the effect of the deviations in pH values during the pH adjustment stage on the chemical reactions. The following pH values were investigated during the pH adjustment stages of these three experiments:

Experiment	pH	
VP9	7.10	(High)
VP10	5.47	(Low)
VP11	5.90	(Normal)

During the experiment VP11, the pH was adjusted according to the standard procedure. The above data shows that the pH value was increased by 19% during the experiment VP9 whereas it was decreased by 7% during the experiment VP10. Because of fears of gelation pH values below 5.47 were not investigated.

During these experiments, except for the pH values, the process conditions and parameters were kept exactly the same. The same 44% formalin was used as a raw material for each of these experiments. The experiments VP9 and VP10 were performed on the same day. The experiment VP11 was performed few days after these two experiments VP9 and VP10. The formalin was stored in an oven at 45 °C during this period.

The acid reaction stage was excluded from the process during these experiments. The objective was to study the effect on the chemical reactions during the dehydration stage. During the experiment VP11, the dehydration stage was extended for about 72 hours. This will be discussed in Section 6.6.

Seven resin samples were taken during each of these experiments; one at the end of the methylolation stage and the other six during the dehydration stage. It was already known from the previous experiments that the chemical reactions mainly occur during the first 80 minutes of the dehydration stage. Therefore, these samples were taken during the first 120 minutes of the dehydration stage. The first four samples during the dehydration stage were taken at the interval of 15 minutes to study the initial reaction rates in detail.

These three experiments were different from the previously reported experiments in two ways. Previously, the 'end of the methylolation stage (1M)' samples were unable to be analysed for their water content because they were insoluble in the methanol used for the Karl Fischer's titrations. The samples taken during this series of experiments were however soluble in methanol and the water content of these samples was measured. The use of the mass balance method was extended to the methylolation stage to investigate the occurrence of the condensation and butylation reactions during this stage.

The resin samples during these experiments were taken more frequently during the early period of the dehydration stage than that for the previous experiments. It was possible to see the gradual changes occurring in solids as a function of reaction time for these three different process conditions. A photograph of these vacuum solids samples was taken and is given in Figure 6.9.

The final results in the form of plots of butyl ether, and methylene ether versus the reaction time were produced from the data reported in the Appendix 4 and are given in Figures 6.10 and 6.11 respectively.

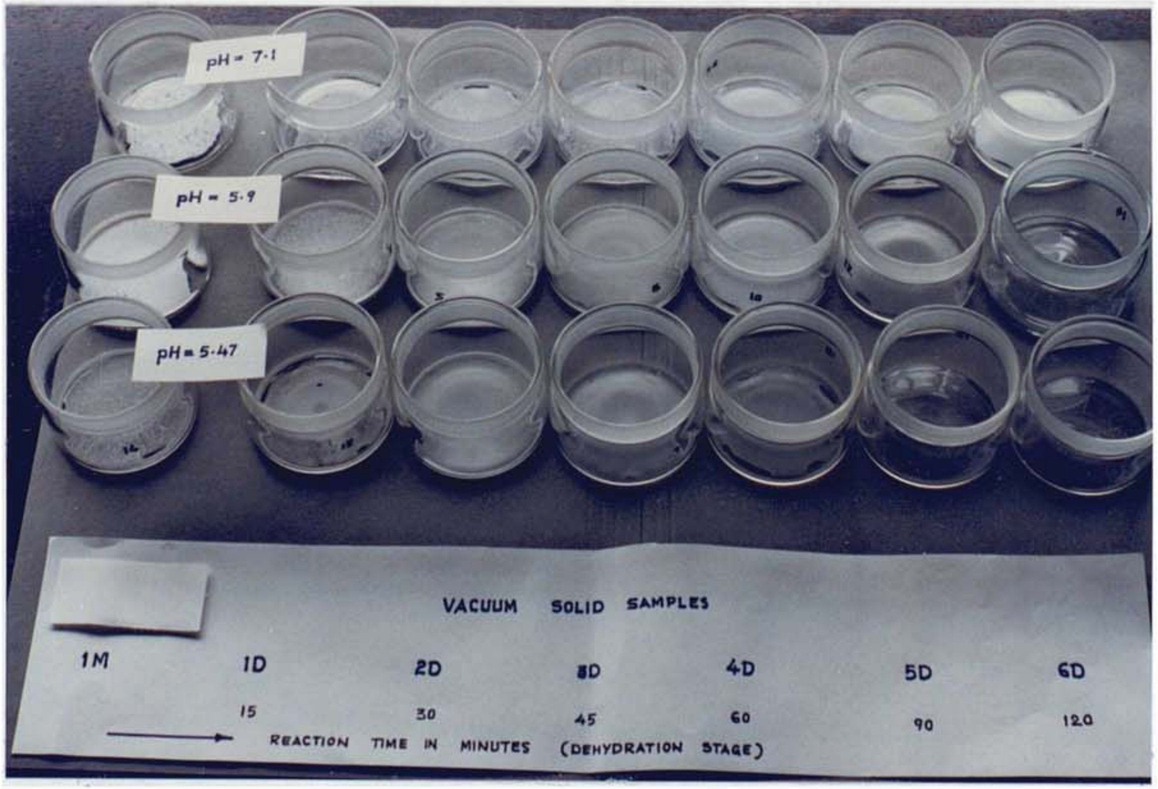


Figure 6.9 A Photograph of Vacuum Solids Samples

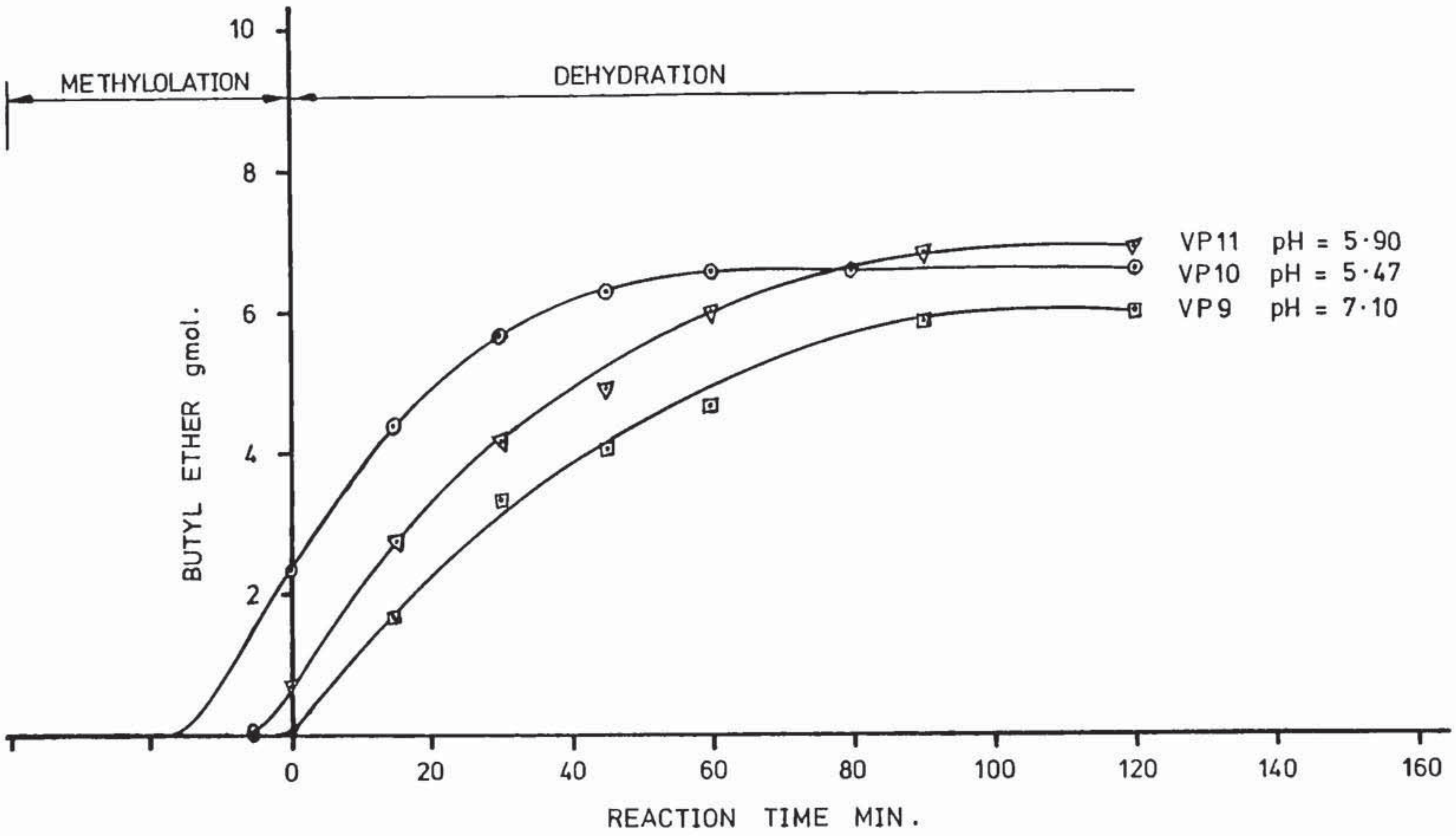


Figure 6.10 Butyl Ether / Reaction Time Plots for the Experiments VP9, VP10 and VP11

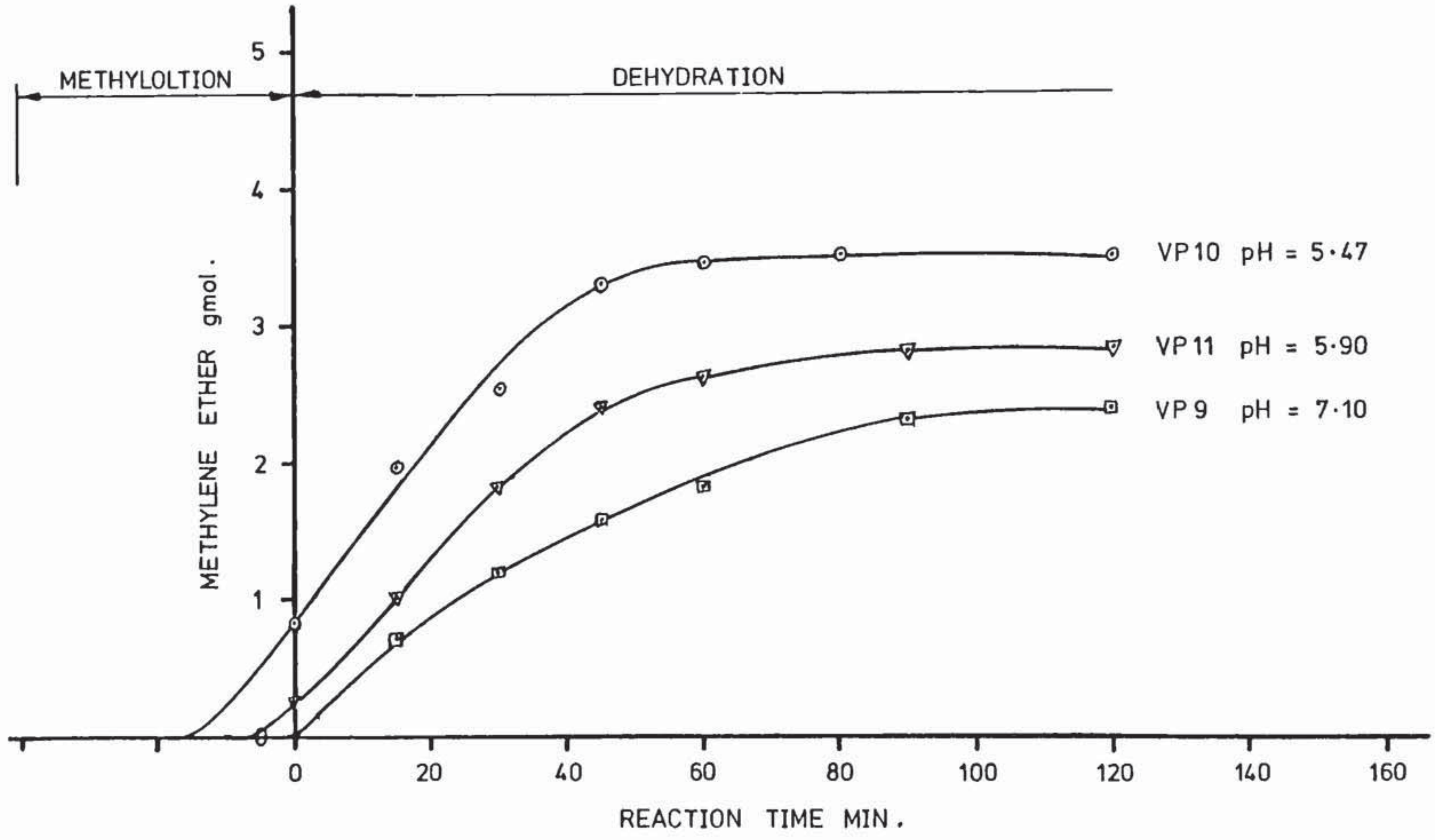


Figure 6.11 Methylene Ether / Reaction Time Plots for the Experiments VP9, VP10 & VP11

6.5.1 Discussion and Conclusions

These three experiments facilitated the study of the effect of pH on chemical reactions occurring, since the other process conditions and parameters were kept constant. This can be seen from the plots of butyl ether and methylene ether versus the reaction time given in Figures 6.10 and 6.11. These plots were produced by using the mass balance method. These differences in product quality can also be seen from the photograph of the vacuum solids samples given in Figure 6.9. This practical evidence supports the results determined by the mass balance method.

During these experiments, the water content of samples taken at the 'end of the methylolation stage (1M)' was measured and hence the use of the mass balance method was extended to the methylolation stage. This revealed useful information regarding the condensation and butylation reactions occurring during the methylolation stage.

In the experiment carried out at a pH of 7.1, the condensation and butylation reactions did not occur during the methylolation stage. When a pH of 5.47 was used, the condensation and butylation reactions occurred to a considerable extent during the last 15 minutes of the methylolation stage. At this point, 2.31 gmoles of butyl ether and 0.82 gmoles of methylene ether bridges were produced. Under normal processing condition (pH 5.9), the condesation and butylation reactions occurred only to a small extent during the last 5 minutes of the methylolation stage.

Figures 6.10 and 6.11 illustrate the above conclusions. The physical appearance of the vacuum solids samples at the end of the methylolation stage supports these conclusions. Figure 6.9 shows that there is a small physical difference between the vacuum solids sample 1M for the higher pH, 7.1 and that for the normal pH, 5.9. On the other hand there is a considerable physical difference between the vacuum solids sample 1M for the lower pH, 5.47 and that for the normal pH, 5.9.

The degree of methylolation or addition was not affected by the changes in pH. The quantities of unreacted free formaldehyde at the end of the methylolation stage were found nearly the same for these three experiments. Table 6.31 shows the data regarding the combined formaldehyde and the degree of methylolation.

Table 6.31 Degree of addition : Experiments VP9, VP10 and VP11

Experiment No.	Formaldehyde Reacted	Degree of Methylolation
VP9	645.32	3.99
VP10	646.55	3.99
VP11	645.62	3.99

Figures 6.10 and 6.11 clearly show the effect of variations in pH on the chemical reactions during these experiments. During the case of normal pH, 5.9 (VP11), both the condensation and butylation reactions occurred during the dehydration. The reactions started at the 35th minute of the methylolation stage. The reaction rates were fast during the first 45 minutes of the dehydration stage. The reaction rates gradually reduced and the chemical changes were negligible after 80 minutes of the dehydration stage.

In the case of high pH, 7.1 (VP9), the reactions did not start during the methylolation stage and thereafter they occurred at a slower rate than that of the normal case. Less butyl ether groups and methylene ether bridges were produced than in the normal case. This means that under these process condition the reactants were less reactive than in the normal case.

In the case of the low pH, experiment VP10, the reactions started at the 25th minute of the methylolation stage and they occurred at a higher rate than in the normal case. Under these process conditions, the reactants were very reactive. More methylene ether bridges were produced than in the normal case. However, the butyl ether groups produced were somewhat less than in the normal case. This means that the condensation reaction was dominating the competition of the two reactions. The reaction rates were very fast during the first 35 minutes of the dehydration stage. The reaction rates grudually reduced and the chemical changes were negligible after the 60 minutes of the dehydration stage.

The differences discussed above were based on the results produced by using the mass balance method. Figure 6.9 also shows these differences indirectly in an independent way. The physical appearance of the vacuum solids samples was found to change as the reaction time increased. In this Figure 6.9, the upper row of samples represents the case of high pH, the middle row represents the case of normal pH and the lower row represents the case of low pH.

In the case of normal pH, the physical appearances of the vacuum solids changed from a white layer of solids, mainly methylol melamines as discussed previously, to a transparent layer of solids after 120 minutes (sample 6D) of the dehydration stage. This change occurred gradually, as can be seen from Figure 6.9. After 90 minutes (sample 5D) into the dehydration stage the physical appearance of the vacuum solids was nearly colourless, and totally colourless and transparent for the next sample.

In the case of high pH, the upper row, the physical appearances of the vacuum solids changed gradually from a white layer of solids (methylol melamines) to a somewhat clear but not colourless and transparent layer. This shows that the resin was not condensed and butylated to the required level.

In the case of low pH, the bottom row, the physical appearances of the solid residues showed significant change over a short reaction time. It was discussed earlier that a considerable degree of the condensation and butylation occurs during the methylolation stage in this case. Therefore, this time the first vacuum solids sample 1M is not a uniform white layer but a layer with a scatter of white particles, methylol melamines, methylene ether and butyl ether. This vacuum solids sample seems similar to the vacuum solids samples 1D of the middle row and 2D of the top row. In this case, the physical appearances of the vacuum solids became nearly clear or colourless after 60 minutes (sample 4D) into the dehydration stage. The vacuum solids samples 5D and 6D were totally colourless and transparent.

Thus, Figure 6.9 shows that the reactions occurred at a faster rate in the case of low pH and that ocurred at a lower rate in the case of high pH than the normal case. The conclusions drawn from using the mass balance method were thus supported by this practical evidence.

The following conclusions are drawn for the methylolation and dehydration stages of the normal process:

1. The degree of addition is four.
2. The condensation and butylation reactions do occur to some extent during the later period of the methylolation stage. This has been quantified.
3. At the end of the dehydration stage 2.83 gmoles of methylene ether bridges and 6.82 gmoles of butyl ether groups were produced. Therefore, the average quantities (from experiments VP5, 6 and 11) of methylene ether and butyl ether produced at the end of the dehydration stage were 2.78 gmoles and 8.03 gmoles respectively.

6.6 EXTENDED DEHYDRATION STAGE

The previous experimental results showed that the chemical reactions mainly occur during the first eighty minutes of the dehydration stage. The chemical changes occurring during the rest of the dehydration stage are very small. When the acid catalyst is added, the condensation and butylation reactions start occurring with high rates again. The chemical changes mainly occur during the first 120 minutes of the acid reaction stage. It was considered important to investigate what happens when the process is continued without the acid catalyst being added, to check whether further reaction would occur. In order to achieve this objective, the dehydration stage was extended to about 72 hours during the experiment VP11.

During the standard process, the acid catalyst is added when the reaction temperature reaches 102 °C. In this case, the acid catalyst was not added but the water removal process was continued. The second charge of n-butanol was made, but the further additions of n-butanol to control the viscosity were not made. The reaction temperature reached 122 °C during the later stage of this experiment. The volume of total aqueous distillate removed during this experiment was 1456 ml. Three samples of the resin mixture were taken during this extended dehydration stage. Details of the experiment and the mass balance analysis are given in Appendix 4. Plots of butyl ether and methylene ether against the reaction time produced from the mass balance analysis are given in Figures 6.12 and 6.13 respectively.

6.6.1 Discussion and Conclusion

Figure 6.13 shows that a considerable number of methylene ether bridges were produced during the first 20 hours of the extended period. At this stage 3.85 moles of the methylene ether bridges were produced. The amount of methylene ether

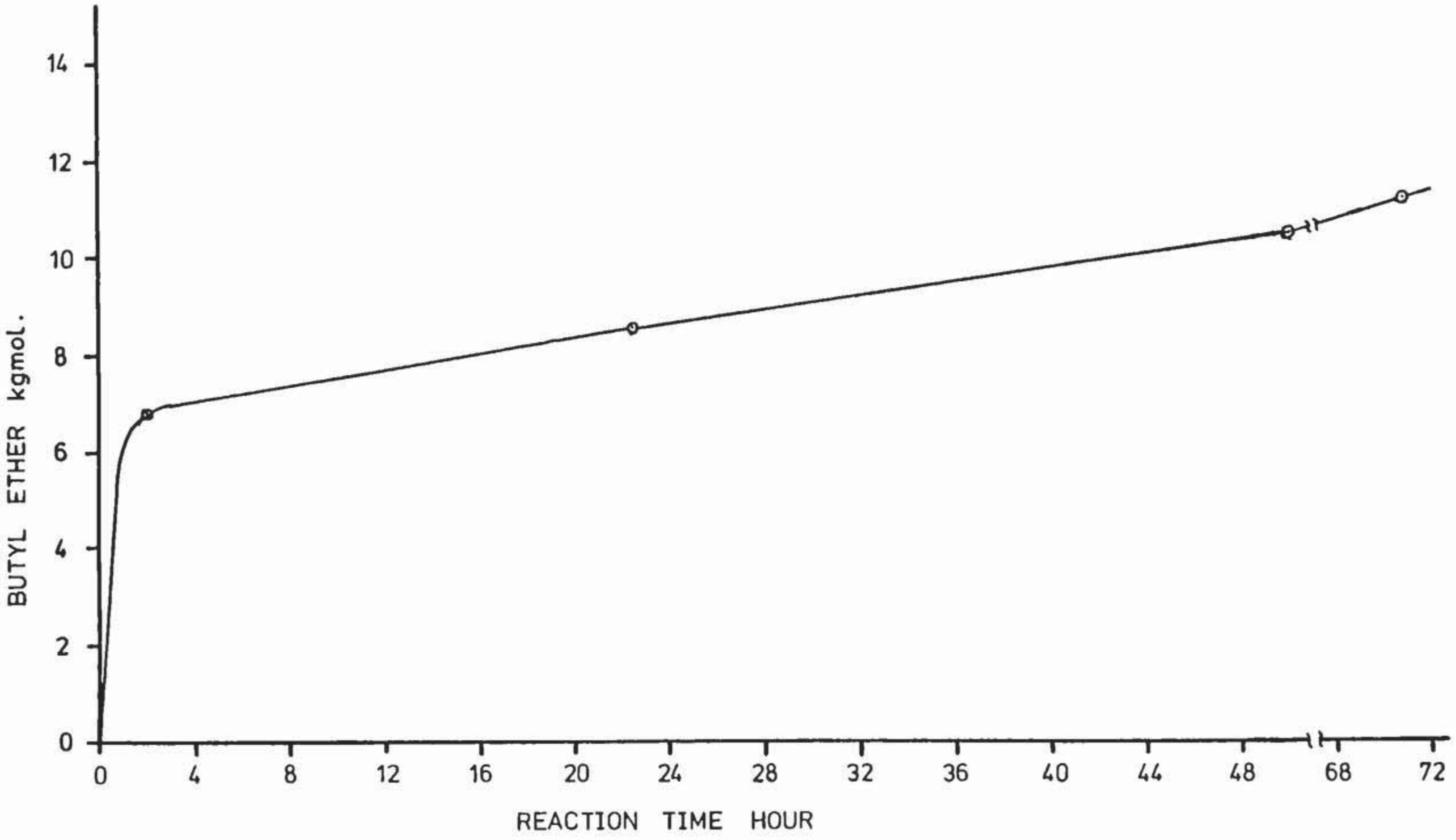


Figure 6.12 Butyl Ether / Reaction Time Plot for the Extended Dehydration Stage of the Experiment VP11

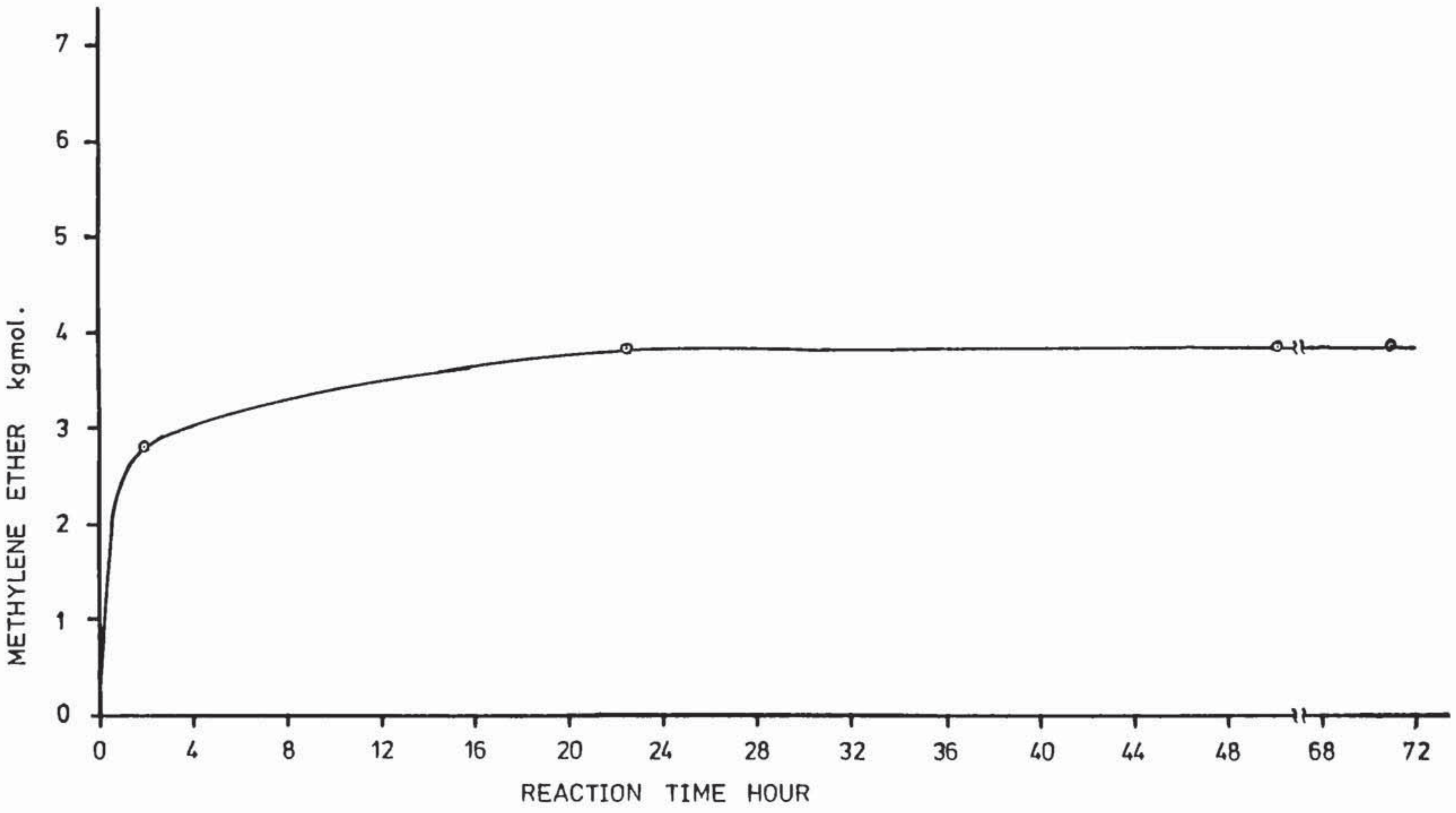


Figure 6.13 Methylene Ether / Reaction Time Plot for the Extended Dehydration Stage of the Experiment VP11

bridges produced during the last 48 hours of the process was negligible. The total amount of the methylene ether bridges produced at the end of the extended process was 3.89 moles. This shows that the condensation reaction did not occur during the last 48 hours of the process. This situation could be explained by one of the two reasons: (a) The reaction stopped for kinetic reasons. Polymer chains are formed by the condensation reaction and hence the resin solution becomes viscous. As a result of this, it becomes extremely difficult for the condensation reaction to go ahead. (b) The reaction is an equilibrium reaction and the equilibrium state was reached. It is not possible to distinguish between these from this experiment.

Figure 6.12 shows that the butylation reaction occurred at a nearly constant rate throughout the extended dehydration stage. This data shows that it was possible for the butanol molecules to react with the methylol groups on the methylol melamines. Hoever, this reaction rate was much smaller than the rate at which the butylation reaction occurred during the first 80 minutes of the dehydration stage.

6.7 PRODUCTION PLANT EXPERIMENTS

Two production scale experiments were carried out on one of the plant reactors at BIP to study the chemical changes occurring during the production process. The mass balance analysis was used for this purpose. These resin batches are coded as Works 1 and Works 2 for this thesis. These batches were of 'Type A' resins, except that in the batch Works 1 the quantity of acid catalyst used was slightly less than the standard quantity (To produce a resin with specific properties). These experiments were to the same formula as the laboratory scale experiments.

Samples of the reaction mixture and the aqueous distillate were collected from these production scale batches. The approximate weights of these samples were considered in the mass balance analysis, although the weights were very small. The aqueous distillate was directed to the AD weigh tank during these experiments. The weight of aqueous distillate removed during each sampling interval was calculated from the readings of the AD weight display meter in the control room.

The molar ratio of materials used during these two batches was according to the standard procedure; formaldehyde: melamine: n-butanol = 5.29 : 1 : 3.89. The quantity of melamine used in these batches was 1075 kilograms or 8.525 kgmoles. During the laboratory experiments the quantity of melamine used was 680 grams or 5.39 gmoles. This represents a scale factor of 1 : 1582 compared with works batches. Details regarding these two plant batches are given in Appendix 4.

The process data given in Appendix 4 shows that the total quantity of aqueous distillate removed during the batch Works 1 was 2371 kilograms whereas the quantity removed during the batch Works 2 was 2547 kilograms. There was a difference of 176 kilograms in the quantities of the aqueous distillate of these two batches. A difference of approximately 70 kg was expected because of the difference in the quantities of the acid catalyst used. The observed difference however was too big to be due to this factor alone. From the laboratory data, the predicted weight of aqueous distillate for the production plant was around 2350 kilograms. This showed that the quantity of aqueous distillate removed during the batch Works 1 was not far from the theoretical, but that it was high for the batch Works 2. The process data given in Appendices 6.9 and 6.10 show that during the batch Works 2 the readings of the aqueous distillate remained high compared to that of the batch Works 1 from the start of the dehydration stage and the difference gradually increased with process time.

Details of the analytical work carried out for these batches are given in Appendix 4. The complete mass balance analysis was carried out for the experiment Works 1 and is given in Appendix 4. For the experiment Works 2, only the mass balances for the solids and n-butanol are given in Appendix 4. The mass balance analysis for the water content was carried out but the resulting data for the water produced was inconsistent because of the erroneous AD weight data. Therefore, it has not been included and no further analysis was carried out. The mass balance analysis for the n-butanol was not affected significantly by the AD data because the n-butanol content of the AD was very small.

The plots of the butyl ether and methylene ether against the reaction time resulting from the mass balance analysis for the batch Works 1 are given in Figures 6.14 and 6.15 respectively. Figure 6.14 also contains the butyl ether versus the reaction time plot for the batch Works 2. The resins produced from these two batches were within the specification.

6.7.1 Discussion and Conclusions

The experimental results show that the mass balance method can be used to study the chemical changes occurring during the production process, provided that the quantitative measurements of the required materials are correct. During the laboratory scale experiments the quantities can be measured accurately, without any source of error. During the plant experiments one has to rely on various automatic instruments for the measurements of the required quantities, and there are possibilities of errors in measurements because of false instrument signal, faulty calibration or data transmission.

Measurement of the aqueous distillate is very important for the mass balance analysis, as it mainly contains water and hence can directly affect the calculation of the quantity of water produced by the butylation and condensation reactions. The water produced by the butylation reaction can be calculated from the reduction in the quantity of n-butanol over a particular process period. This n-butanol quantity is not

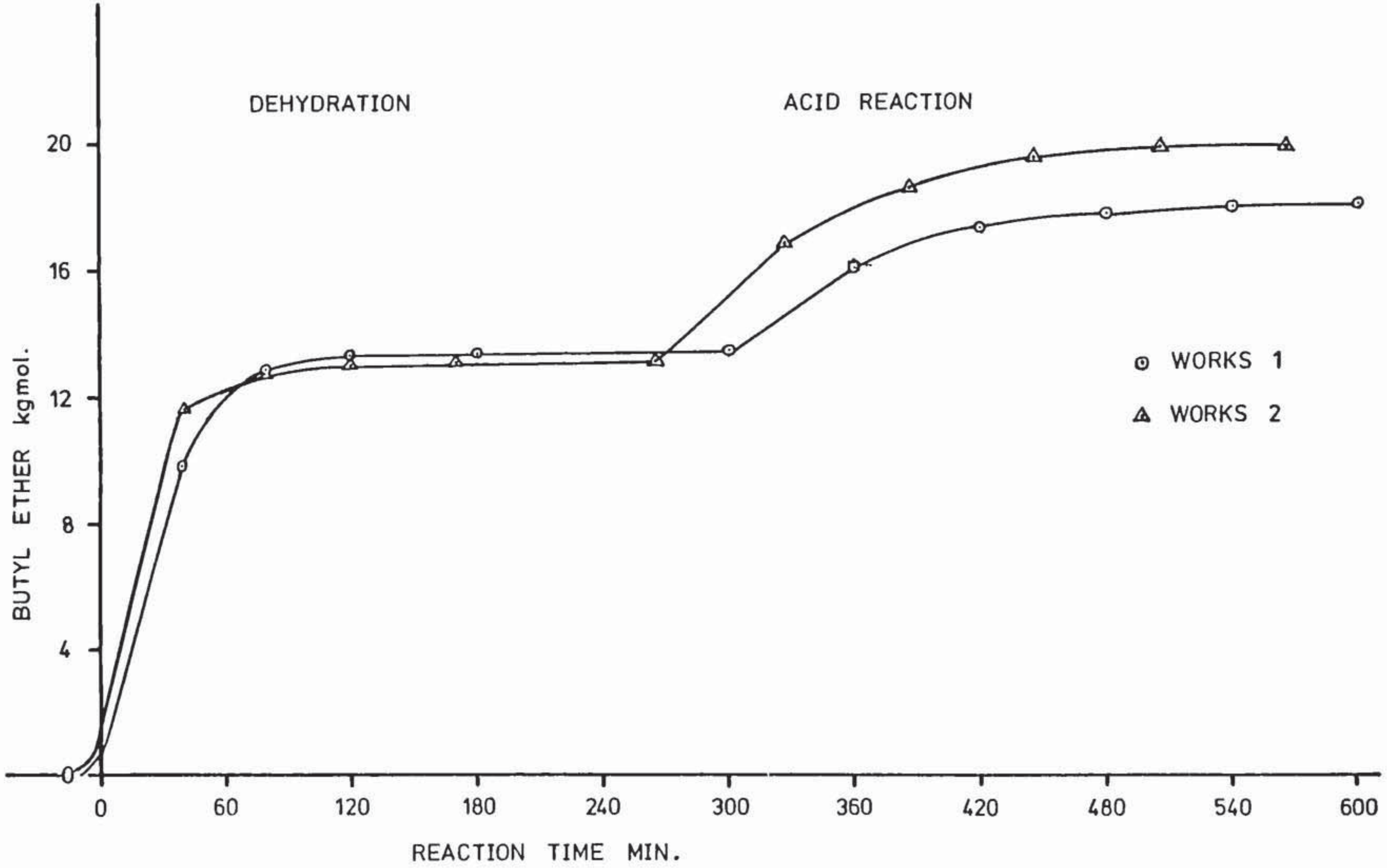


Figure 6.14 Butyl Ether / Reaction Time Plots for the Plant Batches Works 1 and Works 2

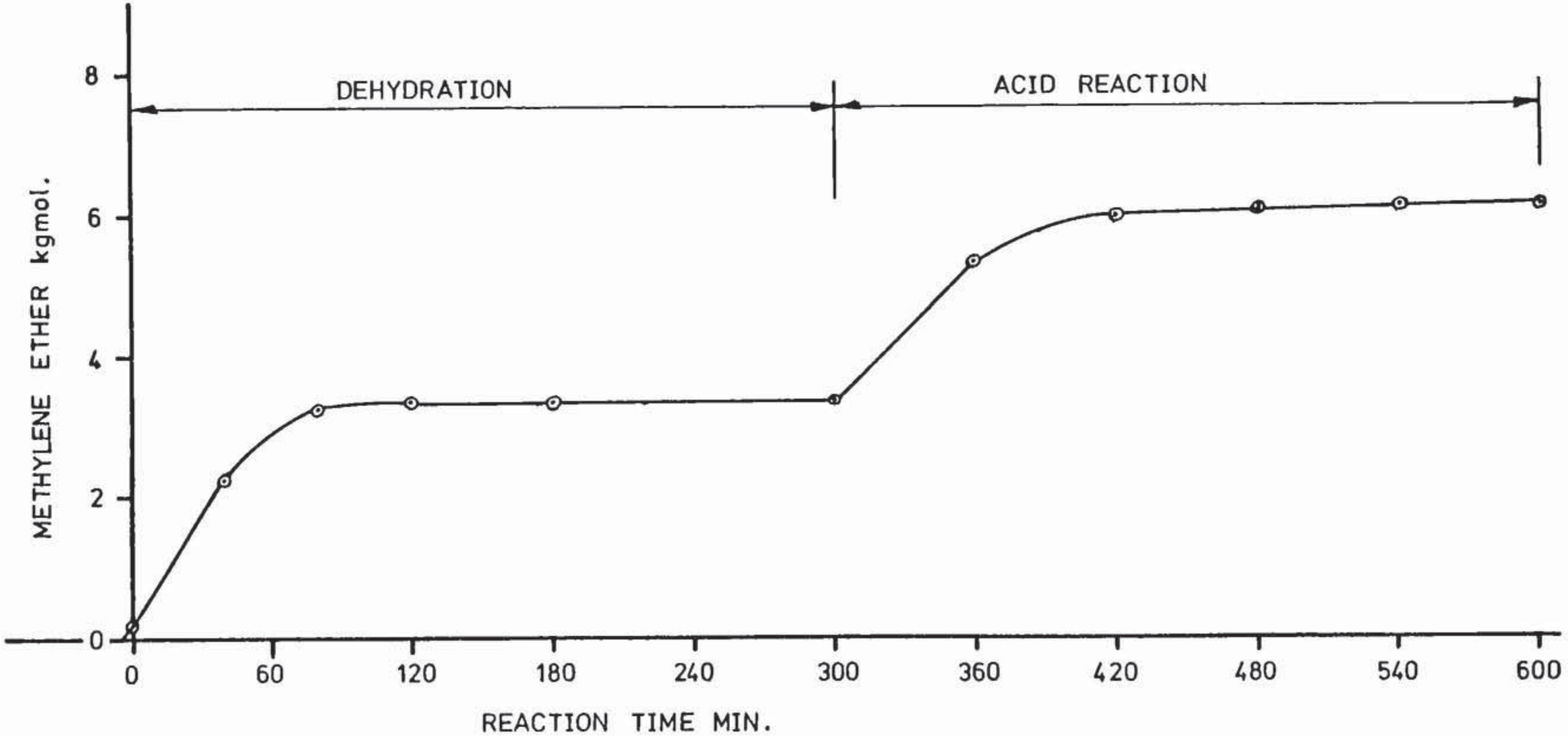


Figure 6.15 Methylene Ether / Reaction Time Plot for the Plant Batch Works 1

significantly affected by errors in the AD measurement, because of the low n-butanol concentration present. That is why it was possible to produce the data of butylation for the batch Works 2.

When the quantity of water produced by the butylation reaction is subtracted from the total quantity of water produced, the rest of the water is considered to have been produced by the condensation reaction. Therefore, the extent of the condensation reaction calculated from the mass balance analysis can be significantly affected by an error in AD measurements. The AD normally contains 85% (Wt) to 90% (Wt) water. Therefore, an error of 20 kg in AD measurement can cause an error of 1 kgmole in methylene ether calculation.

During the production scale experiments Works 1 and Works 2, the quantities of formaldehyde reacted during the methylolation stage were found to be 1012.78 kgs and 1022.51 kgs respectively. Hence the quantities of methylols produced were 33.73 kgmoles and 34.05 kgmoles respectively and the average degree of addition was 3.96 and 3.99 respectively. The condensation and butylation reactions occurred to some extent during the later period of the methylolation stage. These are very similar to the laboratory results for the methylolation stage.

During the dehydration and acid reaction stages, the condensation and butylation reactions occurred simultaneously. The reactions mainly occurred during the first 80 minutes of the dehydration stage and the first 120 minutes of the acid reaction stage. The chemical changes occurred during the remaining periods were very small.

For the batch Works 1, 3.38 kgmoles of methylene ether bridges and 13.42 kgmoles of butyl ether groups were produced at the end of the dehydration stage. At the end of the acid reaction stage, these quantities had increased to 6.13 kgmoles and

18.00 kgmoles respectively.

These quantities can be compared with the laboratory results. It was discussed in the previous section that the scale difference between production batches and laboratory experiments was 1582 : 1. Therefore, the laboratory results expressed in gmoles should be multiplied by 1582/1000 factor to compare them with the plant results expressed in kgmoles.

For the normal laboratory process, the average quantities of methylene ether and butyl ether produced during the dehydration stage were 2.78 gmoles and 8.03 gmoles respectively. This was shown in Section 6.5.1. During the acid reaction stage these average quantities were increased by 1.23 gmoles and 3.66 gmoles respectively. This was shown in Section 6.3.4. Thus, the average quantities of methylene ether and butyl ether produced at the end of the process were 4.01 gmoles and 11.69 gmoles respectively. From this data the predictions for the plant results were as follows:

Dehydration Stage	Prediction	Result obtained
Methylene ether	2.78 x 1.582 = 4.40 kgmoles	3.38 kgmoles
Butyl ether	8.03 x 1.582 = 12.70 kgmoles	13.42 kgmoles
Acid Reaction Stage		
Methylene ether	4.01 x 1.582 = 6.34 kgmoles	6.13 kgmoles
Butyl ether	11.69 x 1.582 = 18.49 kgmoles	18.00 kgmoles

The above discussion shows that the laboratory results can be directly related with the plant results.

It was discussed in Section 4.4.1 that the laboratory scale reactor system was more efficient than the production plant. The processing time of the plant experiments was slightly longer than that of the laboratory experiments. However, the results showed that the reaction rates were not significantly affected. This demonstrates that resin products with the same qualities can be produced on different plants with different batch times varrying from 12 to 19 hours, depending upon the plant efficiencies.

6.8 GENERAL DISCUSSION

The mass balance method described in Chapter 5 was used to obtain data regarding the chemical changes occurring during the process. The method was based on the assumptions that methanol and xylol do not take part in the chemical reactions occurring during the process. The experimental results show that these assumptions are satisfactory. During the mass balance analysis, the n-butanol quantities were not measured but calculated by difference. However, the mass balance method was found to be an adequate and reliable method for studying the chemical changes occurring during the process. The theoretical and experimental quantities of solids produced were compared and the figures agreed within the experimental errors.

There can be two sources of errors for the mass balance method, (a) sampling error and (b) error in the quantitative measurements or calculation of the components involved. The sampling error was discussed in Section 6.3.2. A reaction mixture sample must be representative sample of the reaction system, while sampling from the reactor or while taking it out from the sample bottle for the analysis.

The analysis of the experimetal results has improved the understanding of the chemical reactions occurring during the process. The results have been used for modelling the important process stages. This is discussed in Chapter 7. The overall discussion and conclusions are given in Chapter 8.

CHAPTER SEVEN

ANALYSIS OF KINETIC DATA

7.1 INTRODUCTION

The previous chapter dealt with the collection of kinetic data for the chemical reactions occurring during the three important process stages, methylolation, dehydration and acid reaction. Mathematical models have been produced for these stages and the stages were simulated using the kinetic data. These models are discussed in this chapter.

7.2 METHYLOLATION STAGE

It was discussed very briefly in Section 2.3.1.1 that the methylolation model reported by Aldersley et al [9] was tested against the more precise and reliable data published by Tomita [10]. New values of the model parameters, N_g and N_l were found as a result of this model fitting. The modified model was then used to simulate the methylolation stage of the process, allowing for changes in the process conditions. The simulation is discussed in detail in the following sub-sections.

7.2.1 The Methylolation Model reported by Aldersley et al

The methylolation model reported by Aldersley et al [9] was discussed in Sections 2.3.1 and 2.3.1.1 while discussing the chemistry of the addition reaction. The model consists of eleven differential equations and is shown in Table 7.2. The reaction scheme for the model was shown in Figure 2.2. The terms used in the model are explained in Table 7.1.

Table 7.1 Terms used in the methylolation model

C_0 = Concentration of melamine
C_F = Concentration of free formaldehyde
C_1 to C_9 = Concentrations of methylol melamines 1 to 9
F = Molar ratio of formaldehyde to melamine
k_1 = Second order forward rate constant
k_2 = First order backward rate constant
N_g = Genral substitution effect
N_l = Local substitution effect

Aldersley et al [9] studied the addition reaction by analysing free formaldehyde concentrations as a function of reaction time. The following process conditions were used for their study.

Temperature = 45 °C constant
pH = 9.5 constant
Formaldehyde/Melamine, Molar ratio = 5

The initial concentrations of formaldehyde and melamine used were 0.2747 mol/l and 0.055 mol/l respectively. The plot of their experimental free formaldehyde concentrations against the reaction time is shown in Figure 7.1. The following rate constants and model parameters were determined by them for the optimum fit to their experimental results.

K = 0.2208 mol/l Equilibrium constant
k_1 = 1.412 l/mol.hr
k_2 = 0.3118 1/hr
N_g = 1
N_l = 0.61 ± 0.03

In fact they found $N_g = 1.011$ for the optimum fit, but afterwards they concluded that the general substitution effect is negligible and can be neglected, i.e. $N_g = 1.0$.

Table 7.2 The methylolation model [9]

Using these rate constants and model parameters, the methylolation model was solved on a Harris 800 computer using the 'SIMLIB' simiulation library to fit the experimental data. The Aston Simulation Program (ASP) produced by Gay and Payne [40] was modified and converted to FORTRAN 77 from BASIC. (The modified program was compiled and the compiled version was stored in a library named 'SIMLIB' on a Harris 800 computer.) The Runge Kutta method of the 'SIMLIB' library was used to integrate the differential equations. The model solution included the concentrations of free melamine, free formaldehyde and nine possible methylol melamines. The plots of the experimental and the model, free formaldehyde concentrations against the reaction time are shown in Figure 7.1. The model solutions were also achieved by changing the parameter N_1 ($N_1 = 0.59$ and 0.63), but the best fit values were obtained using $N_1 = 0.61$.

Thus, the methylolation model reported by Aldersley et al [9] was confirmed and the algorithm used to solve the model was verified.

7.2.2 Testing The Model Against Tomita's Data

Tomita [10] studied the addition reaction by direct observation with NMR spectroscopy and high speed liquid chromatography. This was discussed in Section 2.3.1.1. He used a liquid chromatographic technique for the quantitative analysis of methylol melamines in the reaction mixture.

The experiment which was carried out at 45 °C, using the molar ratio of formaldehyde to melamine (F/M) equal to 5 was chosen for the model fitting for two reasons; firstly, the molar ratio was nearly equal to that used in the works procedure and secondly, the process conditions were nearly the same as that used by Aldersley et al. The process conditions for both the experiments are given as follows.

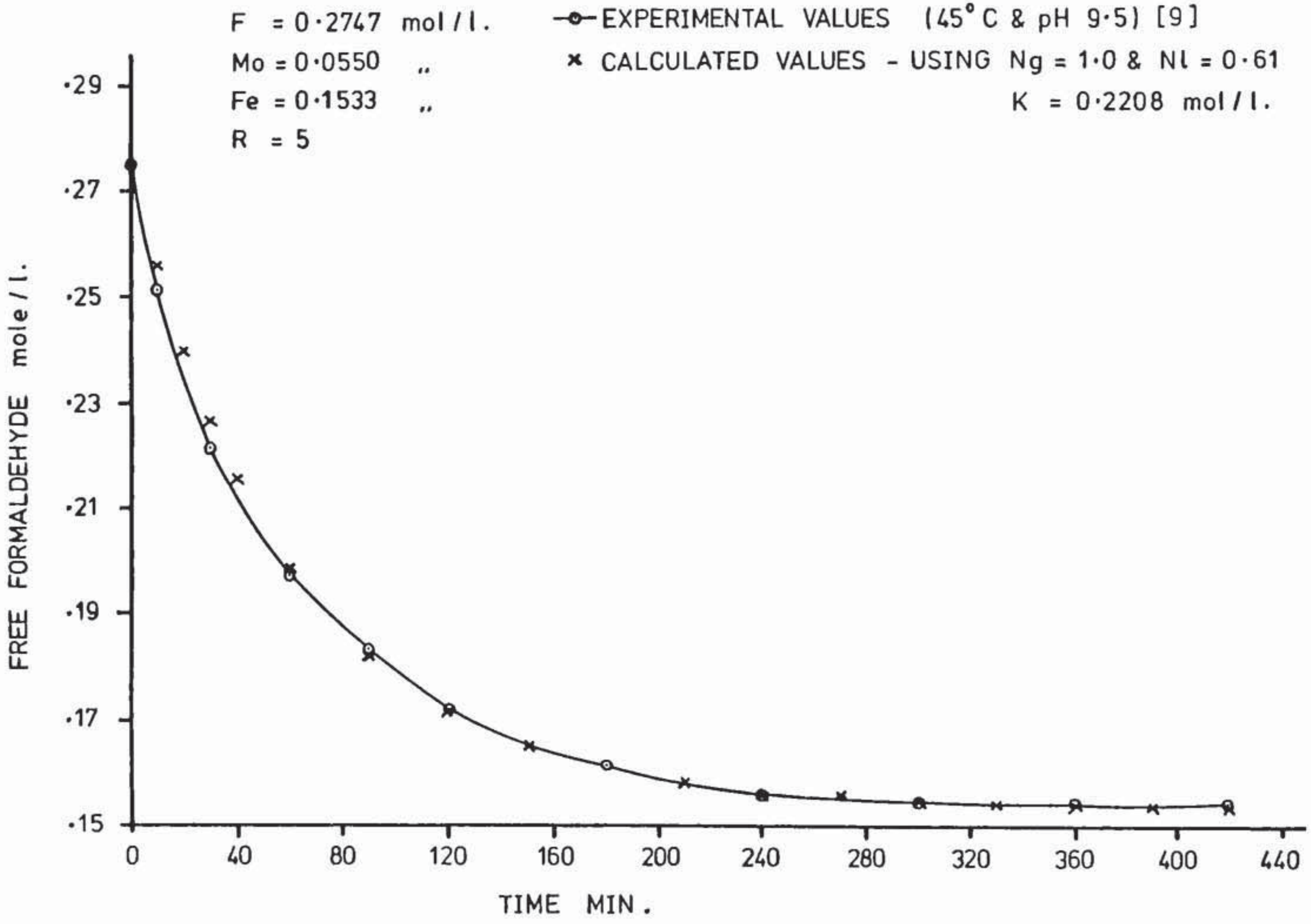


Figure 7.1 Free Formaldehyde Concentration / Reaction Time Plot

Tomita : Temperature = 48 °C, pH = 9.0, F/M = 5.
Aldersley et al : Temperature = 45 °C, pH = 9.5, F/M = 5.

The experimental results reported in terms of plots by Tomita [10] are shown in Figure 7.2. The initial concentrations of formaldehyde and melamine used were 0.167 mol/l and 0.0325 mol/l respectively. Concentrations of free melamine and six methylol melamines, 1 to 6 were measured and reported in these results as functions of time. This set of experimental data provided a good opportunity to test the model. Previously, the model was based on the free formaldehyde analysis and the measurement of free formaldehyde is subject to some uncertainty. Tomita determined the free formaldehyde contents of the reaction mixtures by iodine-sulphite, ammonium chloride and potassium cyanate titration methods. These methods were extremely time consuming and produced results of questionable reliability and the need for a more reliable method was suggested. The molar concentration of free formaldehyde at the equilibrium state was determined using the liquid chromatographic technique.

This availability of data from Tomita for compounds other than formaldehyde gave a very good opportunity to test the model against seven more precise variables instead of one variable as a function of time.

The model was solved using the optimum rate constants and model parameters reported by Aldersley et al [9], but the model results did not fit with the Tomita's experimental results. The parameter N_1 was varied between 0.63 and 0.59 during two more simulation runs, but the model results still did not provide a satisfactory fit with the experimental data.

Therefore, the model parameters N_g and N_l were changed to get a solution which matched the experimental data. By trial, the best fit model parameters were found empirically to be:

$N_g = 0.93$ and $N_l = 0.59 \pm 0.03$

Using the new model parameters ($N_g = 0.93$ and $N_l = 0.59$) and the old rate constants $k_1 = 0.0235$ l/mol.min and $K = 0.2208$ l/mol, it was found that the calculated reaction rates were faster than the experimental rates. Hence the forward rate constant k_1 was reduced, keeping the equilibrium constant the same. Best calculated values which nearly match with the experimental values were found using the following combination:

$N_g = 0.93$ $K = 0.2208$ l/mol

$N_l = 0.59$ $k_1 = 0.016$ l/mol. min

The computer print out showing the concentrations of all eleven components at each ten minutes interval, is given in Appendix 5. The plots of concentration versus time for the calculated values of free melamine and methylol melamines are given in Figure 7.2 which also contains the plots of the experimental values. Tomita [10] did not report the free formaldehyde concentrations as a function of time, however, the equilibrium concentration after 24 hours of free formaldehyde reported was 0.110 mol/l. The model solution showed that the changes in free formaldehyde concentration became negligible after five hours and the concentration at the 330th minute was 0.116 mol/l.

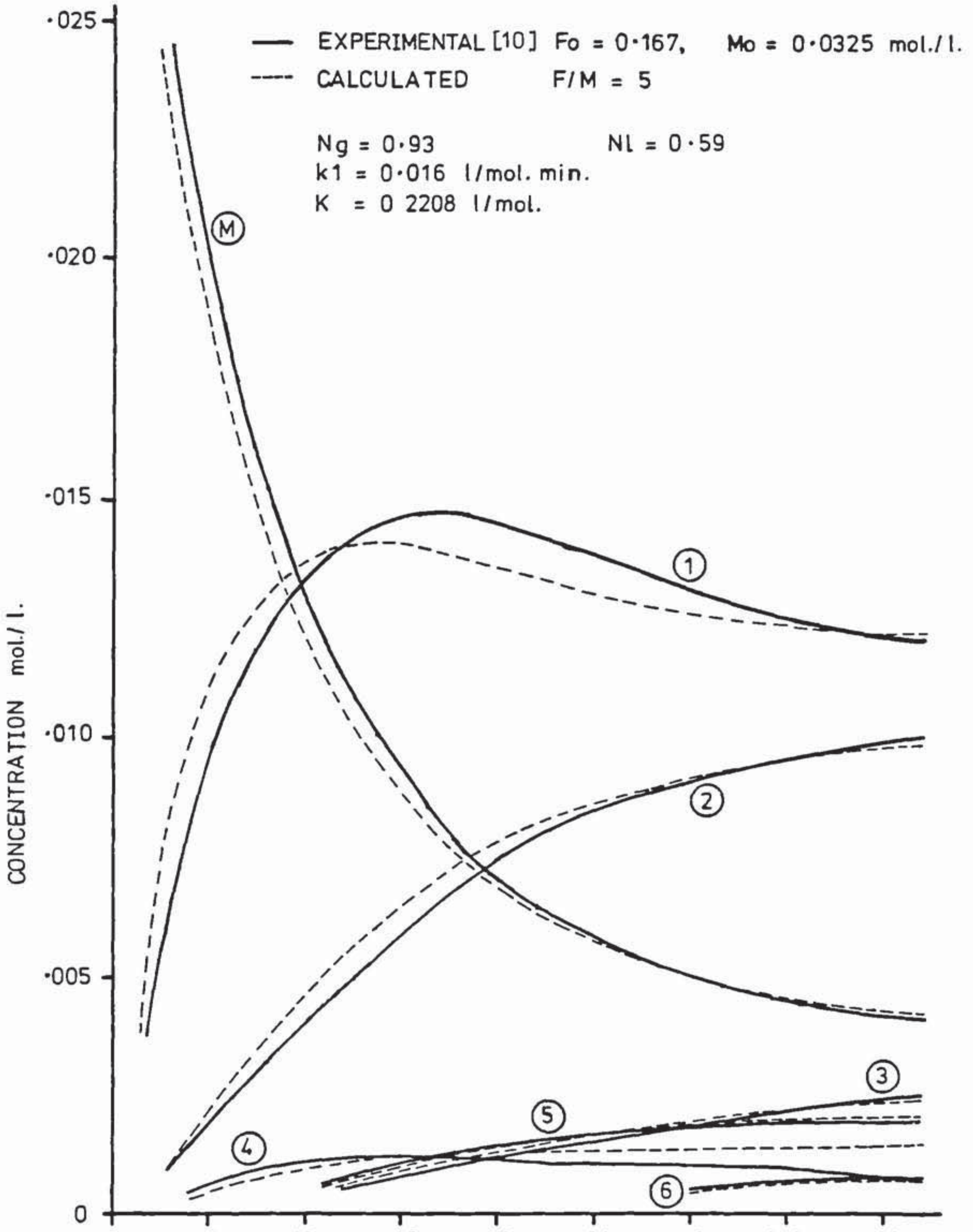


Figure 7.2 Concentration / Reaction Time Plots for Methylols and Melamine.

New values of the model parameters, N_g and N_l were found as a result of this model fitting. Previously the general substitution effect was neglected by Aldersley et al [9] and the parameter N_g was considered to be 1.0. During this model fitting, the value of the parameter N_g found was 0.93. This revealed an important fact that a significant general substitution effect was also present but it was much less than the local substitution effect, as the parameter N_l was equal to 0.59.

This work showed that the combination of the model of Aldersley et al with the revised parameters based on the data of Tomita [10] provided a basis for the modelling of the methylolation stage. If this model could be used to predict the progress of laboratory resin batches, then no further analysis of this stage of the process would be required.

7.2.3 Simulation of The Methylolation Stage

Experimental results for the methylolation stage were discussed in Sections 6.2 and 6.2.1. The temperature versus the reaction time plot was shown in Figure 6.1. The methylolation model discussed up to now has been only for a constant temperature process. In order to simulate the methylolation stage, the model has been modified in two ways; firstly to allow for the temperature changes occurring during the stage and secondly, to allow for the effect on the rate constants of the variation of temperature during the stage.

From the experiment VP2, temperature was found to be a function of the reaction time. The plot in Figure 6.1 was modelled with three discrete rates of temperature change at different stages of the reaction. During the first 5 minutes, the temperature rose with a slope of 0.80 °C/min. During the next 5 minutes, it rose with a slope of 2.2 °C/min. During the period from 10 to 25 minutes, the temperature rose with a slope of 3.333 °C/min. and after that it remained constant at 94 °C. The computer program for the simulation was written using the three rates of change.

The rate constants as a function of reaction temperature were considered using the Arrhenius plot of rate constants published by Gordon et al [8]. The Arrhenius plot of ln k versus (1/T) x 1,000, where T is equal to the absolute temperature in °K, is shown in Figure 7.3. The following logic was used in the computer program to solve the rate constants.

```
TINV  =  1000/(TEMP + 273)                        For any temperature TEMP °C
T0INV =  1000/(T0 + 273)                          For the initial temperature, 28 °C
ln k1 =  ln k01 + Slope 1 x (TINV - T0INV)
ln k2 =  ln k02 + Slope 2 x (TINV - T0INV)
$k_1$    =  EXP (ln k1) x 60
$k_2$    =  EXP (ln k2) x 60
```

From the previous best fit exercise, it was considered that values of rate constants reported by Aldersley et al [9] and Gordon et al [8] were high, so a function which can produce somewhat lower rate constants was used to solve the model. However, the calculated reaction rates were found much faster than the experimental reaction rates.

Many combinations of ln k01, ln k02, Slope 1 and Slope 2 were tried to get the better simulation result. The following combination was found best after trials on the basis of visual approximations.

ln k01 = - 12.35 Slope 1 = - 11.85
ln k02 = - 14.00 Slope 2 = - 12.60

As a result of this simulation the Arrehenius plot of rate constant was modified and is given in Figure 7.3. The model solution (computer print out) and the computer program are given in Appendix 5. The plot of free formaldehyde concentrations versus the reaction time is given in Figure 7.4, which also contains the plot of the experimental values. A visual comparison between the calculated values and the experimental values can be made. The model solution included the concentrations of free melamine, free formaldehyde and nine possible methylol melamines. From this data, the plots of methylol melamines against the reaction time were prepared and are shown in Figure 7.5.

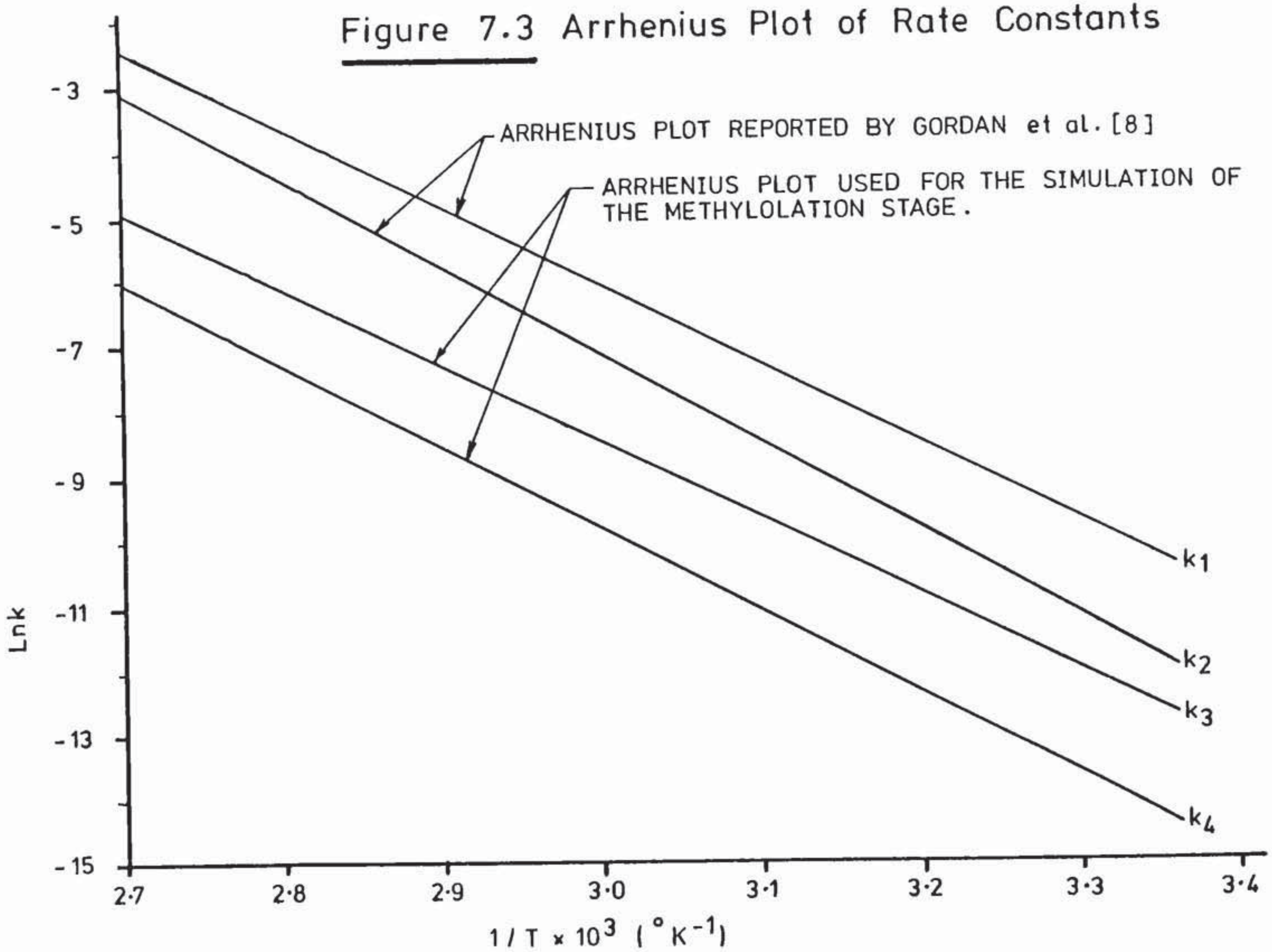
7.3 DEHYDRATION AND ACID REACTION STAGES

The butylation and condensation reactions as shown in Section 5.2 occur during the dehydration and acid reaction stages, producing the butyl ether groups and the methylene ether bridges respectively. Experimental data on these chemical species with respect to the reaction time were produced using the mass balance method. This was discussed in Chapter 6. Except for this data, there was no kinetic data available on these reactions either at BIP or in the literature.

It was shown in the previous section that nine methylol melamines with different compositions can be produced as a result of the addition reaction occurring during the methylolation stage and the reaction rates are affected by two substitution effects.

During the dehydration and acid reaction stages, the situation becomes even more complex as these nine methylol melamines are involved in two competing parallel reactions, butylation and condensation. The volume of the reaction mixture changes during these stages, as the aqueous distillate is removed continuously from the reactor, and at intervals further butanol additions are made.

Figure 7.3 Arrhenius Plot of Rate Constants



ARRHENIUS PLOT REPORTED BY GORDAN et al. [8]

ARRHENIUS PLOT USED FOR THE SIMULATION OF THE METHYLOLATION STAGE.

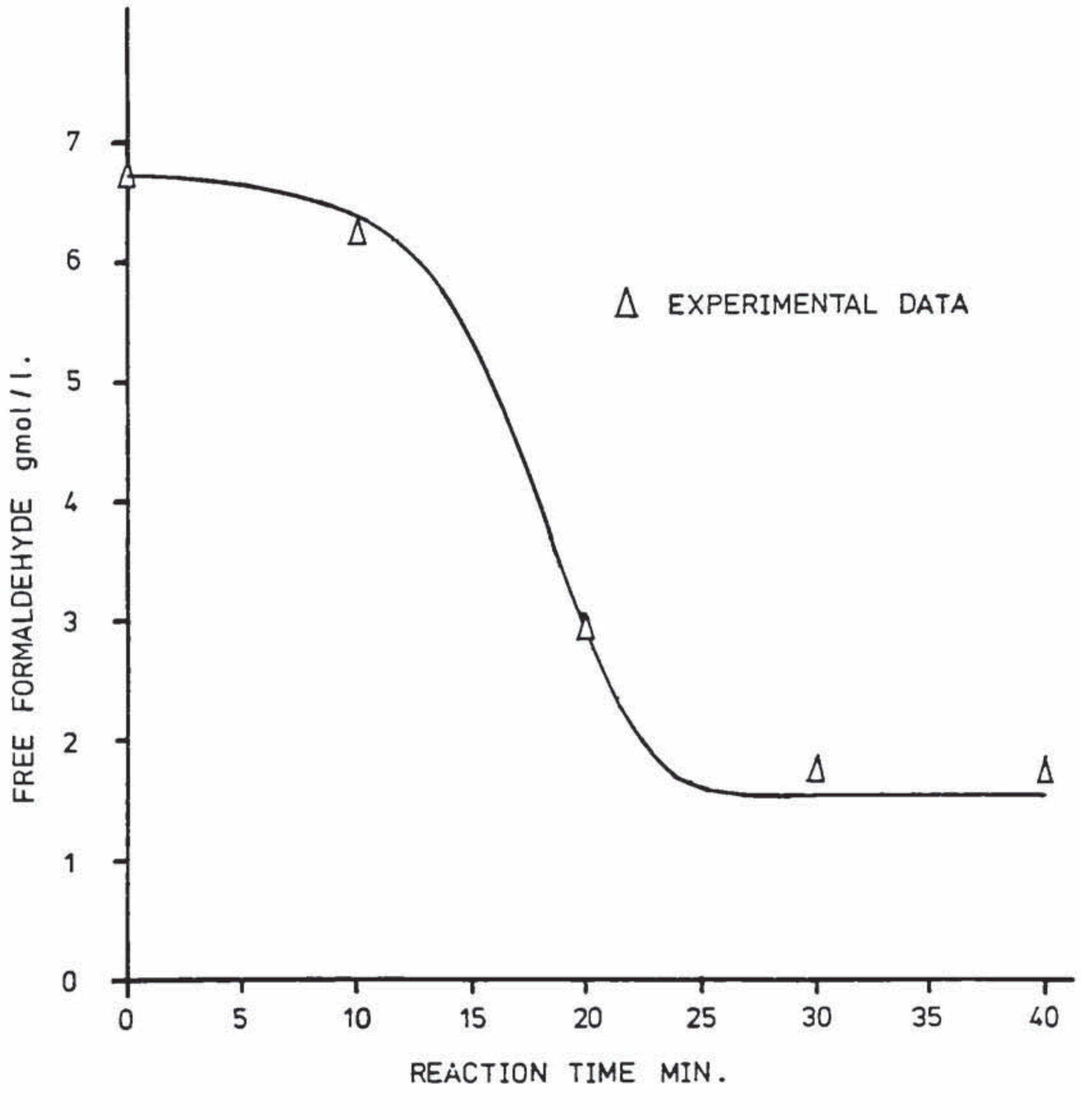


Figure 7.4 Simulation of the Methylolation Stage

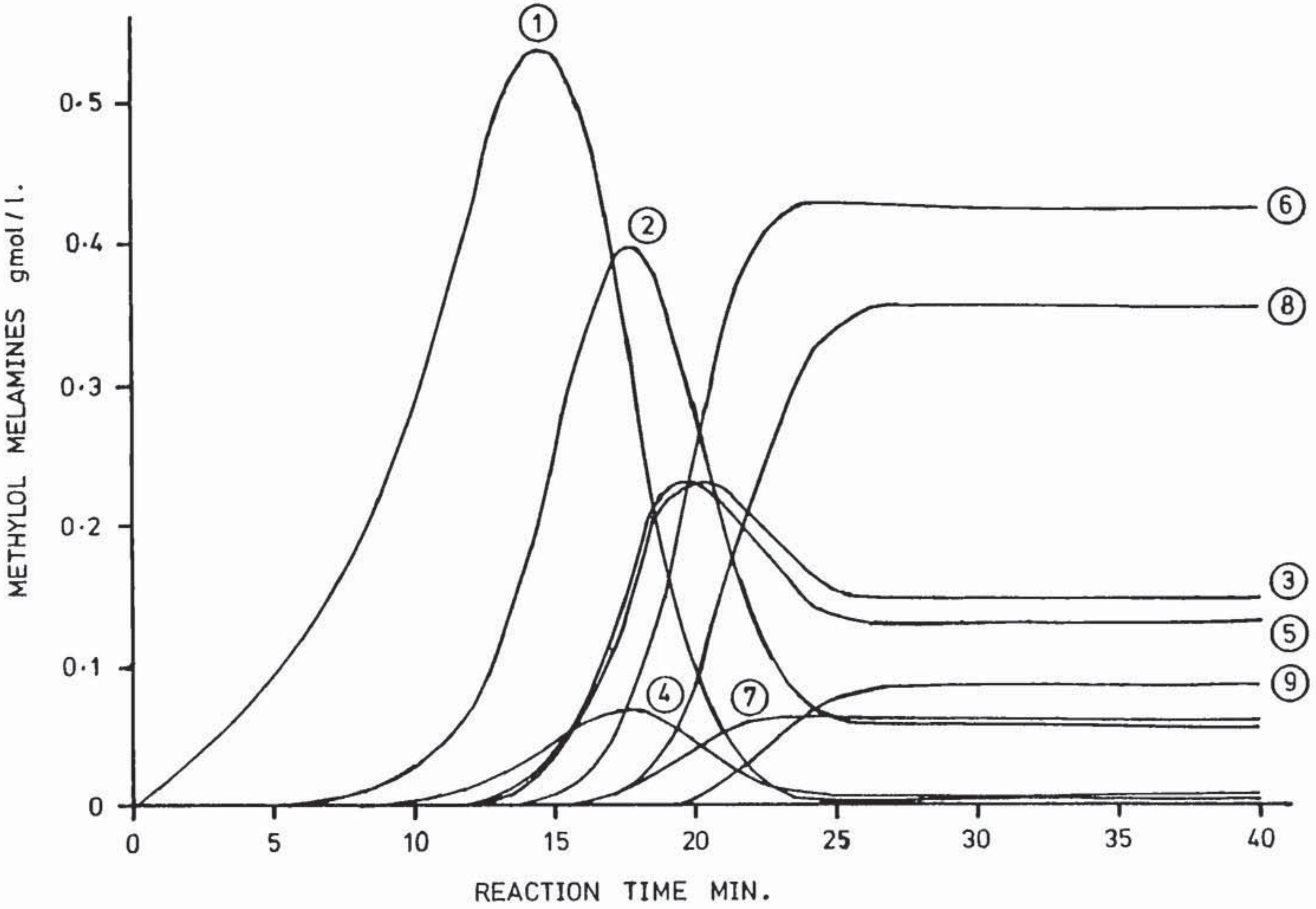


Figure 7.5 Methylol Melamines / Reaction Time Plots

Before considering analysis of the experimental results, the following discussion is presented of possible factors affecting the reaction rates of butylation and condensation.

The rates of these reactions are likely to be affected by the substitution effects previously mentioned in the context of methylolation in Chapter 2. The two effects can be defined as follows. (a) Local effect : If one methylol group of a particular nitrogen atom on a melamine nucleus is already butylated or condensed, the reactivity of the second methylol group (considering both the hydrogen atoms to be methylolated) will be less than that of the first one. (b) General effect : If 'r' (r = 1,2,....5) methylol groups of a melamine nucleus are butylated or condensed, then the reactivity of the 'r + 1' methylol will be less than that of the previous one. The reaction rates are also affected by the polymerization process. The reactivity of a polymer molecule reduces with the increase in its chain length. Because of all these complexities it was not possible to produce a model in terms of rate equations, as it was done for the methylolation stage.

Experimental results regarding the changes in the chemical species as a function of time were available as molar quantities and not as the concentrations. Empirical rate equations are generally written to express the concentration changes as a function of time. From the analysis of experimental kinetic data using an appropriate empirical rate equation, the rate constants and the order of a reaction are determined approximately.

Empirical regression equations based on the experimental data were produced using a simple mathematical model. This is discussed in the following sub-sections.

7.3.1 Model Selection

Himmelblau [41], in his book, 'Process Analysis by Statistical Methods' presented plots of five non-linear models while discussing the problem of selecting a model. These plots were examined and compared with the experimental plots to find a representative model. Visual selection was possible as the shapes of the plots were easily distinguishable from each other. The following model was selected as a result of this process.

$$X \text{ or } Y = \beta_1 + \beta_2 \, (1 - e^{-\beta_3 t}) \qquad \text{......(7.1)}$$

where X = Butyl ether group in moles

Y = Methylene ether bridges in moles

t = Reaction time in minutes

β_1 = Initial values of X or Y in moles

β_2 = Parameter responsible for the elevation of a plot. This can be also written as $\beta_s - \beta_1$, where β_s is the steady state or final value of X or Yin moles.

β_3 = Parameter responsible for the shape of a curve, units of which are 1/min. In other words it is the first order rate constant, k.

Using $\beta_1 = X_0$ or Y_0,

$\beta_2 = X_1$ or Y_1, or $(X_s - X_0)$ or $(Y_s - Y_0)$

and $\beta_3 = k$,

the butylation model becomes:

$$X = X_0 + X_1 \, (1 - e^{-kt}) \qquad \text{......(7.2)}$$

or

$$X = X_0 + (X_s - X_0)(1 - e^{-kt})$$

$$X = X_s - (X_s - X_0)\,e^{-kt} \qquad \text{......(7.3)}$$

Similarly, the condensation model becomes:

$$Y = Y_0 + Y_1 (1 - e^{-kt}) \qquad \text{......(7.4)}$$

or

$$Y = Y_s - (Y_s - Y_0)\,e^{-kt} \qquad \text{......(7.5)}$$

Equations, 7.2 to 7.5 are the integrated forms. The rate equations of which can be derived by differentiating them as follows.

For the butylation model, the rate equation becomes,

$$\frac{dX}{dt} = 0 + 0 - (-k)(X_1)e^{-kt}$$

$$= k(X_1)e^{-kt} \qquad \text{......(7.6)}$$

or, using (7.2)

$$\frac{dX}{dt} = k(X_s - X) \qquad \text{......(7.7)}$$

Similarly, for the condensation model, the rate equation becomes,

$$\frac{dY}{dt} = k(Y_1)e^{-kt} \qquad \text{......(7.8)}$$

or

$$\frac{dY}{dt} = k(Y_s - Y) \qquad \text{......(7.9)}$$

Equations 7.5 to 7.9 show that chosen model corresponds to the butylation and condensation reactions which are first order in X (butyl ether) and Y (methylene ether) respectively.

After selecting the model, the next step was to determine the model parameters which generate values which give the best fit with the experimental results. This was done separately for the butylation and condensation data for the experimental results of the dehydration and acid reaction stages.

The amounts of butyl ether X_0 and methylene ether Y_0 produced at the start of the dehydration and acid reaction stages were known. The values of X_1 and Y_1 were also known from the experimental results. The rate constants, β_3 or k, for butylation and condensation reactions occurring during the dehydration and acid reaction stages were determined by obtaining the optimum fits with the experimental results, using data from extra samples in the early stages of each reaction.

A single variable, direct search method, the Golden Section Search [42] with the criterion of minimizing the sum of square of errors, was used for this purpose. A computer program written in FORTRAN 77 for the optimization is given in Appendix 5. The computer program was meant to optimize the parameter β_3, however it was also possible to adjust the parameter β_2 to improve the overall fit. This was done as follows.

For each model, the program was run several times using different values of β_2 and the sum of square of errors produced by these runs were scanned manually to find its minimum value. The value of β_2 thus found for each model was used for the final simulation run.

7.3.2 Simulation of the Dehydration and Acid Reaction Stages

Using the data from the experiments VP5 and VP6 separately, empirical equations for the condensation and butylation models of the dehydration and acid reaction stages were produced. This was achieved as follows.

For the experiment VP5, at the start of the dehydration stage, no butyl ether groups were considered to be present, and at the end of the stage, the total amount of butyl ether groups present was 8.36 gmoles. Therefore, the parameter β_1 or X_0 was equal to zero and the parameter β_2 or X_1 was approximately 8.36. The range 0.01 to 0.09 was used for the parameter β_3 or k.

The program was run several times using different values for the parameter β_2 ranging from 8.33 to 8.36. Some of the results produced are given in Table 7.3 to illustrate how the sum of square of errors was minimized to adjust the parameter β_2.

The optimum values of the parameters β_2 and β_3 thus found were 8.339 and 0.0486 respectively. The corresponding sum of square of errors was 0.0011. The results produced by the simulation run is displayed in Table 7.4.

Thus, the empirical equation for the butylation model for the dehydration stage of the experiment VP5 was found to be as follows:

$$Y = 0.0 + 8.339\,(1 - e^{0.0486\,t}) \qquad \text{......(7.10)}$$

Using the similar procedures, empirical equations for the butylation and condensation models of the dehydration and acid reaction stages of both the experiments VP5 and VP6 were produced. The model parameters thus determined are given in Tables 7.5 to 7.8.

The rate constants determined from the results of the experiments VP5 and VP6 for the dehydration stage are not included in Figures 7.6 and 7.7 given in the next section to show the effect of pH on the rate constant. This was because the experiments VP5 and VP6 were not sampled during the early period of the dehydration stage. The chemical reactions mainly occur during this early period.

Therefore, the rate constants determined using the data from the experiments VP5 and VP6 may not be accurate.

On the other hand, during the experiments VP9, VP10 and VP11, the reactions were studied in detail during the early period of the dehydration stage. This was discussed in Section 6.5. The same formalin (44% Wt) solution was used during these experiments. All other process conditions except pH were the same. Therefore, only the rate constants determined from the results of these experiments were considered for the comparison purpose.

Table 7.3 Optimization of the parameter $ß_2$

No.	$ß_1$	$ß_2$	$ß_3$	Sum of square of errors
1	0.00	8.360	0.0472	0.002083
2	0.00	8.340	0.0486	0.001106
3	0.00	8.335	0.0490	0.001099
4	0.00	8.341	0.0485	0.001118
5	0.00	8.339	0.0486	0.001097

Table 7.4 Simulation run : Butylation during the Dehydration stage of the Experiment VP5

Time min	Butyl Ether Experimental gmol	Butyl Ether Model gmol
0	0.0000	0.0000
80	8.1700	8.1688
160	8.3100	8.3355
240	8.3600	8.3389

Table 7.5 Model parameters : Butylation during the Dehydration stage

Experiment	ß$_1$	ß$_2$	ß$_3$	Sum of square of errors	No. of points considered
VP5	0.00	8.339	0.0486	0.0011	4
VP6	0.00	8.826	0.0566	0.0143	4

Table 7.6 Model parameters : Condensation during the Dehydration stage

Experiment	ß$_1$	ß$_2$	ß$_3$	Sum of square of errors	No. of points considered
VP5	0.00	2.650	0.0696	0.00019	4
VP6	0.00	2.845	0.0513	0.00004	4

Table 7.7 Model parameters : Butylation during the Acid Reaction stage

Experiment	ß$_1$	ß$_2$	ß$_3$	Sum of square of errors	No. of points considered
VP5	8.36	4.305	0.0137	0.1716	5
VP6	8.91	3.543	0.0146	0.0940	6

Table 7.8 Model parameters : Condensation during the Acid Reaction stage

Experiment	ß$_1$	ß$_2$	ß$_3$	Sum of square of errors	No. of points considered
VP5	2.66	1.071	0.0269	0.0006	5
VP6	2.85	1.515	0.0139	0.0371	6

7.3.3 Effect of pH on the Rate Constants

The effect of pH on the chemical reactions occurring during the dehydration stage was studied during the experiments VP9, VP10 and VP11. This was discussed in Section 6.5.

Using the data from these experiments, empirical equations for the condensation and butylation models of the dehydration stage were produced using the optimum fits. The model parameters thus determined are given in Table 7.9 and Table 7.10 for the butylation and condensation models respectively. The rate constant against the pH profiles for the butylation and condensation models are shown in Figures 7.6 and 7.7 respectively.

Figures 7.6 and 7.7 show that the rate constant increases with the decrease in pH and the rate of increase becomes rapid below the normal pH value 5.9.

Table 7.9 Effect of pH on the rate constants : Butylation model for the Dehydration stage

Experiment	pH	β_1	β_2	β_3 or k	Sum of square of errors	No. of points considered
VP9	7.10	0.00	6.555	0.0219	0.1699	7
VP10	5.47	2.31	4.371	0.0467	0.0496	7
VP11	5.90	0.68	6.668	0.0243	0.1786	7

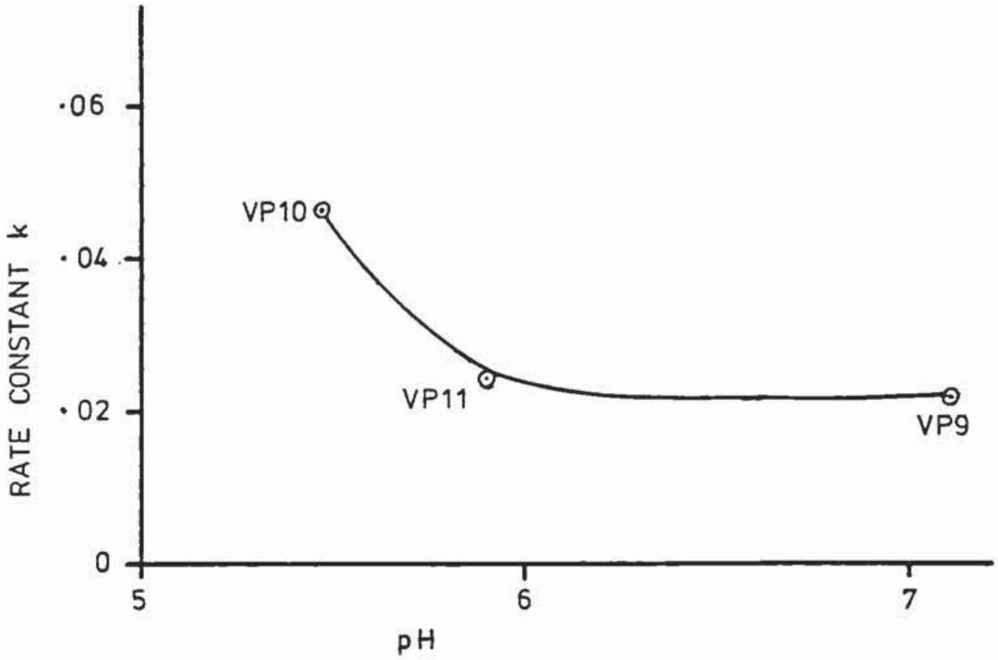


Figure 7.6 Rate Constant / pH Plot for Butylation during the Dehydration Stage

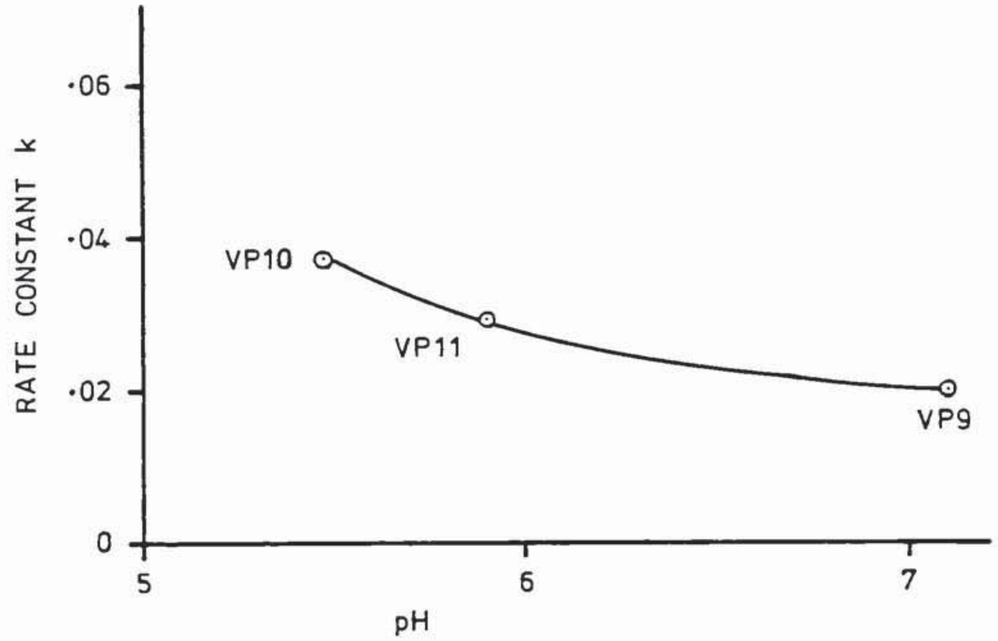


Figure 7.7 Rate Constant / pH Plot for the Condensation during the Dehydration Stage

Table 7.10 Effect of pH on the rate constants : Condensation model for the Dehydration stage

Experiment	pH	β_1	β_2	β_3 or k	Sum of square of errors	No. of points considered
VP9	7.10	0.00	2.736	0.0196	0.0140	7
VP10	5.47	0.82	2.825	0.0375	0.1027	7
VP11	5.90	0.28	2.740	0.0292	0.1089	7

7.4 DISCUSSION

The simulation of the methylolation stage has improved the understanding of the addition reaction including the substitution effects. The model results displayed in Figure 7.5 show that all nine possible methylol melamines as shown in Figure 2.2 are produced during this stage. The concentrations of mono, di and hexamethylol melamines are very small whereas the concentrations of tri, tetra and pentamethylol melamines as labled 3, 5 (isomer of trimethylol melamine), 6 and 8 in Figure 2.2 are significant. This shows the complexity of the process for the butylation and condensation reactions and gives some hints regarding the structure of the resin product. The concentration of tetramethylol melamine, labelled 6, is the highest. The average degree of addition is about 4. The butylation and condensation reactions occurring during the later period of this stage have not been included in the model for this stage.

The dehydration and acid reaction stages were simulated separately for the condensation and butylation reactions producing empirical rate equations. The rate constants determined for these rate equations may not be reliable as they were based on limited experimental data during the early periods of these stages. Further experimental work is required to verify these rate constants.

The rate constants for both the condensation and butylation models were found to be dependent on pH. They increase with the decrease in pH and the increment becomes rapid below the normal pH value 5.9. Further experimental work is required to explore the effect over a wide range of pH and hence to verify the proposed reaction mechanisms for the condensation and butylation reactions.

CHAPTER EIGHT

DISCUSSION AND CONCLUSIONS

8.1 INTRODUCTION

The last three chapters have dealt with the collection and analysis of experimental data regarding the chemical changes occurring during the process. The results were discussed and the conclusions were drawn separately for each section. This chapter deals with the overall discussion and conclusions of this investigation. In addition to that, future work is identified and recommended.

8.2 DISCUSSION

The basis on which this investigation started was described in the Introduction and included a number of distinct objectives. These were:

(1) To devise an indirect method for the analysis of the chemical groups involved and hence to investigate the chemistry involved in the process.

(2) To improve the understanding of the reactions taking place throughout the stages of the batch process.

(3) To develop a model for the batch production of butylated M-F resins.

It was possible to study the methylolation reaction on the basis of free formaldehyde analysis, however it was not possible to study the condensation and butylation reactions as direct quantitative methods were not available for the analysis of the chemical species involved.

An indirect method, termed 'Mass Balance Method' was developed for this purpose, described in Chapter 5. The method was based on the assumptions that methanol and xylol do not take part in the chemical reactions occurring during the process. These assumptions were verified during the applications of this method. During the mass balance analysis, the n-butanol quantities were not measured but calculated by difference. There can be two sources of errors for the mass balance method, (a) sampling error and (b) error in the quantitative measurements or calculations of the components involved. However, the mass balance method was found an adequate and reliable method for studying the chemical changes occurring during the process because the results produced by it were cross-checked by comparing the quantities of experimental solids and the relevant theoretical solids within the experimental errors.

The sampling error was discussed in Section 6.3.2. A reaction mixture sample must be a representative sample of the reaction system, while sampling from the reactor or while taking it out from a sample bottle for the analysis. The precautions to be taken during the quantitative anlysis of the required components were discussed in Section 5.3.

The methylolation stage was studied by free formaldehyde anlysis and solids analysis. The addition reaction between formaldehyde and melamine reached an equilibrium state after 25-30 minutes of the 40 minutes allowed for the reaction. The degree of addition was found to be around 4. That means on average four methylols ($-CH_2OH$) were formed per melamine molecule.

The non-random methylolation model reported by Aldersley et al [9] was fitted to the more precise and reliable data produced by Tomita [10]. This was discussed in Chapter 7. The model parameters, N_g and N_l for the general and local substitution effects respectively, were modified as a result of this fitting. Aldersley et al [9] neglected the general substitution effect considering the parameter N_g to be

1.0. During this work, the value of N_g was found to be 0.93. This revealed an important fact that a significant general substitution effect was also present, but it was much less than the local substitution effect, as the parameter N_l was equal to 0.59. The modified model was used to simulate the methylolation stage considering the changes in the process conditions. This yielded the concentrations of all nine methylol melamines and revealed the complexity of the process.

It was assumed initially and confirmed later, that the condensation and butylation reactions do not occur significantly during the methylolation stage under normal conditions. Later it was found that these reactions can occur to an extent during the last period of the stage depending upon the pH of the reactants at this stage. In case of an experiment with low pH, considerable condensation and butylation occurred during the last 15 minutes of the methylolation stage. In the case of the process with high pH, these reactions did not occur at all during this stage. The overall degree of addition was not affected by the variations of pH or of the butanol concentration.

During the dehydration and acid reaction stages the condensation and butylation reactions occur. There was no relevant data regarding these reactions, either at BIP or in the literature. The process chemistry was poorly understood for these stages. At BIP, the condensation reaction was considered to be occurring in two ways, producing methylene bridges and methylene ether bridges. It was also believed that condensation was the main reaction during the dehydration stage and butylation was the main reaction during the acid reaction stage. The acid reaction stage was generally known as an etherification stage. These views were found to be wrong as a result of this investigation.

It was proved in Section 2.4.2.2 as a result of the ^{13}C NMR analysis, that the condensation reaction occurs in only one way producing methylene ether bridges and not methylene bridges. This was also confirmed by the experimental results produced by the mass balance analysis. The experimental results showed that both the condensation and butylation reactions occur simultaneously during the dehydration and acid reaction stages. In fact more than 60% of the total butylation occurred during the dehydration stage.

The chemical reactions mainly occurred during the first 80 minutes of the dehydration stage and the first 120 minutes of the acid reaction stage. The chemical changes during the remaining periods were found to be very small and the main change occurring was the removal of water from the reactor system. This explains the fact that resin products with the same qualities can be produced on different plants with different batch times varrying from 12 to 19 hours, depending upon the plant efficiencies. The experimental results show that after the first 80 minutes of the dehydration stage, the reactions occur at very slow rates. They occur at faster rates when the acid catalyst is added at the start of the acid reaction stage.

The dehydration and acid reaction stages were simulated using a simple mathematical model. Empirical rate equations were produced for the condensation and butylation reactions. The rate constants and the order of reactions were determined approximately. Both the condensation and butylation reactions were found to be of first order.

The effect of variations in pH on the chemical reactions occurring during the dehydration stage was discussed in Section 6.5.1. The rate constants were found to be dependent on pH. The rate constant increased with the decrease in pH and the increament was found sharp below the normal pH value, 5.9. Thus, pH was found an important process parameter.

Butanol acts as a reactant as well as solvent for the system and is generally maintained in excess. In the competing reaction system, if the quantity of butanol used is considerably less than the standard quantity, then there is a possibility of resin product to be under-butylated and over-condensed. On the other hand, if the quantity used is considerably more than the standard quantity, then there is a possibility of resin product to be over-butylated and under-condensed. The effect of variations in n-butanol concentration was studied and discussed in Section 6.4. During these experiments, the other process conditions except n-butanol concentrations were not the same. No significant effect was found. Small variations showed that reaction rates did not vary with butanol.

This investigation showed from experimental variability the importance of the process materials and process conditions at the start of the three important process stages, methylolation, dehydration and acid reaction. They should be monitored and controlled carefully as they are mainly responsible for the quality of resin product.

The average quantities (from experiments VP5, 6 and 11) of methylene ether and butyl ether produced during the dehydration stage of the normal laboratory process were 2.78 gmoles and 8.03 gmoles respectively. During the acid reaction stage these quantities were increased by 1.23 gmoles and 3.66 gmoles (from experiments VP5 and VP6) respectively. Therefore at the end of the process, the quantities of methylene ether and butyl ether produced were 4.01 gmoles and 11.69 gmoles respectively. During the dehydration stage the ratio of the extent of butylation to condensation was 2.89 and it was 2.92 at the end of the acid reaction stage. Thus there is a greater reaction of butanol with methylol groups than reaction between two methylol groups of two methylol melamines. The laboratory results were confirmed with plant scale experiments. This was discussed in Section 6.7.1.

The above laboratory results were for a process where the quantity of melamine used was 5.39 gmoles. At the end of the process, the quantities of methylene ether and butyl ether produced per gmole of melamine used were 0.74 gmole and 2.17 gmoles respectively. It was shown previously that at the end of the methylolation stage, about four gmoles of methylols are produced per gmole of melamine used.

Therefore, out of these 4 methylols per melamine molecule, 2.17 were butylated and 1.58 were condensed to produce methylene ether bridges (two methylols are required to produce a methylene ether bridge). Thus 0.25 unreacted methylol remained on average on each melamine molecule.

The degree of polymerization was found to be about four. This can be explained as follows. One methylene ether bridge is required to produce a dimer, with two melamine molecule and that means 1/2 or 0.5 methylene ether is required per melamine molecule. Similarly, three methylene ether bridges are required to produce a tetramer, with four melamine molecule and that means 3/4 or 0.75 methylene ethers are required per melamine molecule. It was already shown that 0.74 gmoles of methylene ether were produced per gmole of melamine at the end of the process. Thus, averagely tetramers are produced as a result of the polymerization process.

8.3 CONCLUSIONS

The following important conclusions have been drawn from this investigation:

1. It is possible to perform laboratory experiments reproducing the full scale plant process and reliably produce resins with the specified quality. Thus the bench scale experiment can be satisfactorily used for the study of the plant process.
2. The mass balance method described is an adequate and reliable method for studying the chemical changes occurring during the process. This has been shown for both the laboratory scale and plant scale experiments.

3. **Methylolation Stage**

   (i) The addition reaction reaches an equilibrium state within the methylolation stage, and all nine possible methylol melamines are produced with different compositions.

   (ii) The degree of addition or methylolation is 4. This means on average four methylol groups are produced per melamine molecule.

   (iii) During the addition reaction, a significant general substitution effect is present, but it is much less than the local substitution effect.

   (iv) The condensation and butylation reactions occur to an extent during the later part of this stage, with a dependence on pH, the extent increasing as pH is decreased.

4. **Dehydration and Acid Reaction Stages**

   (i) The understanding of the competing consecutive chemical reactions occurring during these stages has been improved.

   (ii) The condensation and butylation reactions as shown in Section 5, occur simultaneously during these stages. The condensation reaction produces only methylene ether bridges and not methylene bridges.

   (iii) The chemical reactions occur mainly during the first 80 minutes of the dehydration stage and the first 120 minutes of the acid reaction stage. Water removal from the reactor is the main activity during the remaining periods of these stages as the chemical changes involved in them are very small.

   (iv) At the end of the process, on average 0.74 mole of methylene ether bridges and 2.17 moles of butyl ether groups are produced per mole of melamine by the condensation and butylation reactions respectively. Hence, on average 0.25 mole of unreacted methylol groups remain in resin products, per mole of melamine used.

   (v) The degree of polymerization is about 4.

5. The rate constants for the condensation and butylation reactions, increase with

the decrease in pH value and the increment is sharp below the normal pH value 5.9. Therefore, pH is identified as a very important process parameter for product consistency.

6. The reaction rates do not vary significantly with the variations in n-butanol concentration.

8.4 FUTURE WORK

The following areas of work have been identified and recommended as an extension to this work:

(1) To produce an optimum process and plant design to reduce the batch time.

(2) To investigate on-line measuring techniques to improve process control using the information provided by this work.

(3) The mass balance method may be used to study other coating resins.

(4) Further work is needed on kinetics to understand the mechanism.

APPENDICES

APPENDIX 1

EQUILIBRIUM DATA : n-BUTANOL / WATER SYSTEM

Figure A 1.1 Vapour - Liquid Equilibrium Curve for n - Butanol - Water System [34]

Figure A 1.2 Boiling Point - Composition Curve for n - Butanol - Water at 767 mm. [34]

APPENDIX 2

LOG SHEETS OF LABORATORY EXPERIMENTS PV4 TO PV7

Table A2.1 Experimental Detail : PV4

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C PRS	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.79 l Formalin charged
		5.55				1.851 l n-Butanol charged
		6.10				0.08 ml Caustic added
						680 g Melamine charged
						Methylolation
0	27					Heat on
20	96					Boiling commenced
35	96					Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
25	93				150	
55	93				330	
85	93				530	
115	95				725	
175	97		5 -		1090	0.459 l n-Butanol added
195	102		3A		1155	Heat off
						Acid Reaction
						3.794 ml Acid catalyst added
0						Heat on
30	109		6+	6.3	1340	
60	113		9A	9.9	1445	0.250 l n-Butanol added
90	118		6A	15.9	1485	
125	118		6A	21.2	1490	
185	118		7A	25.7	1510	0.050 l n-Butanol added
215	118		7A	30.4	1515	
245	118		8+	32.0	1520	Heat off, Cooling on.
						Solvent Adjustment
						Vacuum equipment set up
0						Vacuum and Heat on
15	79		12 -	31.2		0.325 l wet solvent off
						Vacuum off, Heat off
						Cooling on.

Table A2.2 Experimental Detail : PV5

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C PRS	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.79 l Formalin charged
		5.30				1.851 l n-Butanol charged
		5.80				0.10 ml Caustic added
						680 g Melamine charged
						Methylolation
0	27					Heat on
20	96					Boiling commenced
35	96					Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
25	93				170	
55	93				370	
85	94				560	
115	95				750	
145	96		3		930	
175	99		6 -		1102	0.459 l n-Butanol added
195	103				1160	Heat off
						Acid Reaction
						3.794 ml Acid catalyst added
0						Heat on
35	109		6A	5.7	1340	
65	113		9A -	9.8	1410	0.300 l n-Butanol added
95	114		5A	14.4	1430	
135	122		6	22.4	1475	
195	122		6A	25.4	1490	
225	122		7	27.6	1495	
255	123		8	32.3	1508	Heat off, Cooling on.
						Solvent Adjustment
						Vacuum equipment set up
0						Vacuum and Heat on
20			13A	26.9		0.503 l wet solvent off
						Vacuum off, Heat off
25			12A	30.5		0.173 l wet solvent added
						Cooling on.

Table A2.3 Experimental Detail : PV6

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C PRS	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.79 l Formalin charged
		5.20				1.851 l n-Butanol charged
		6.30				0.11 ml Caustic added
						680 g Melamine charged
						Methylolation
0	27					Heat on
20	96					Boiling commenced
35	96					Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
30	95				260	
60	95				460	
90	95		4		620	0.459 l n-Butanol added
140	95		1A		875	
170	95		2 -		990	
200	99		3A		1170	
230	102		5+		1290	Heat off
						Acid Reaction
						3.794 ml Acid catalyst added
0						Heat on
50	112		10A+		1445	0.300 l n-Butanol added
95	120		8	15.4	1500	
125	120		8A -	20.0	1512	
155	122		8A+	22.4	1525	0.100 l n-Butanol added
185	122		7A+	27.0	1534	
215	122		7A+	29.3	1540	
245	122		8	32.9	1544	Heat off, Cooling on.
						Solvent Adjustment
						Vacuum equipment set up
0						Vacuum and Heat on
20			13+	29.5		0.474 l wet solvent off
						Vacuum off, Heat off
40			12A	29.4		0.050 l wet solvent added
						Cooling on.

Table A2.4 Experimental Detail : PV7

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C PRS	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.79 l Formalin charged
		5.10				1.851 l n-Butanol charged
		5.95				0.10 ml Caustic added
						680 g Melamine charged
						Methylolation
0	27					Heat on
15	95					Boiling commenced
30	95					Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
30	95				245	
60	95				460	
90	95				660	
120	95				855	
150	96		5 -		1050	0.459 l n-Butanol added
170	103		4 -		1175	Heat off
						Acid Reaction
						3.794 ml Acid catalyst added
0						Heat on
45	110		9A+	7.0	1400	0.250 l n-Butanol added
75	118		7A -	13.3	1475	
115	122		8	18.0	1500	
145	122		8A	20.5	1517	0.050 l n-Butanol added
175	122		8A -	24.0	1525	
205	124		8A	25.6	1532	
250	122		9+	30.0	1540	Heat off, Cooling on.
						Solvent Adjustment
						Vacuum equipment set up
0						Vacuum and Heat on
20			12A+	30.0		0.352 l wet solvent off
						Vacuum off, Heat off
40			12A+	29.4		0.025 l wet solvent added
						Cooling on.

APPENDIX 3

ANALYTICAL METHODS

A3.1 Sulphite back titration method to determine free formaldehyde in resin mixtures

Reagents

2 M Sodium sulphite solution
1.0 N Sulphuric acid
1.0 N and 0.1 N Sodium hydroxide
Thymolphthalein indicator (0.04% in alcohol/water)
Absolute alcohol or 74.0 OP Meths

Procedure

Weigh accurately, by difference, from a weighing bottle between 2 and 3 grams of resin into a 500 ml conical flask containing 100 mls of absolute alcohol. Agitate the flask to dissolve the resin. When the resin has completely dissolved in the alcohol, add distilled water until the solution just goes cloudy. Carefully neutralise the cloudy solution with 0.1 N NaOH to thymolphthalein.

Immediately add 10 mls 1.0 N H_2SO_4 from a burette followed by 25 mls neutral sodium sulphite solution. Mix thoroughly then allow to stand for 1minute, then back titrate the excess H_2SO_4 with 1.0 N NaOH using thymolphthalein as indicator. Perform the test two or three times and take the average result.

Calculation

$Na_2SO_3 + CH_2O + H_2O \longrightarrow HOCH_2NaSO_3 + NaOH$
30.03 grams CH_2O = 1000 mls 1.0 N NaOH
% free formaldehyde in sample is given by

$$\frac{\{(10 \times N_1) - (T \times N_2)\} \times 30.03 \times 100}{1000 \times W}$$

W = Weight of sample (grams)
T = Titration mls NaOH
N_1 = Normality of H_2SO_4
N_2 = Normality of NaOH

A3.2 Determination of formaldehyde content of formalin

Reagents

1.0 N and 0.1 N Sulphuric acids
0.1 N Sodium hydroxide solution
Thymolphthalein indicator solution (in alcohol)
1 M Sodium sulphite solution

Procedure

Weigh accurately, by difference, from a syringe about 2 grams of formaldehyde solution into a 250 ml conical flask containing approximately 10ml distilled water. Cover the mouth of the flask with watch glass. Add 75 ml sodium sulphite solution to a second conical flask. Add thymolphthalein (2 drops) to the sodium sulphite solution. Carefully neutralise the sodium sulphite solution with 0.1 N sulphuric acid (blue colour just disappears), and cover the flask with a watch glass.

Add thymolphthalein (2 drops) to the weighed formalin sample. Carefully neutralise the formaldehyde solution with 0.1 N sodium hydroxide solution (indicator turns blue). Add the neutralised sodium sulphite solution to the neutralised formaldehyde solution. Mix it by swirling and leave the mixture for two minutes, keeping the flask shut with a watch glass. When two minutes have elapsed since mixing, titrate the mixture with 1.0 N sulphuric acid until the blue colour just disappears.

Calculation

$$Na_2SO_3 + CH_2O + H_2O \longrightarrow HOCH_2NaSO_3 + NaOH$$

$$\text{Wt \% Formaldehyde} = \frac{3.003 \times T \times N}{W}$$

Where T = Titration mls sulphuric acid
N = Normality of acid used for titration
W = Weight of sample

A3.3 Determination of methanol content of formalin

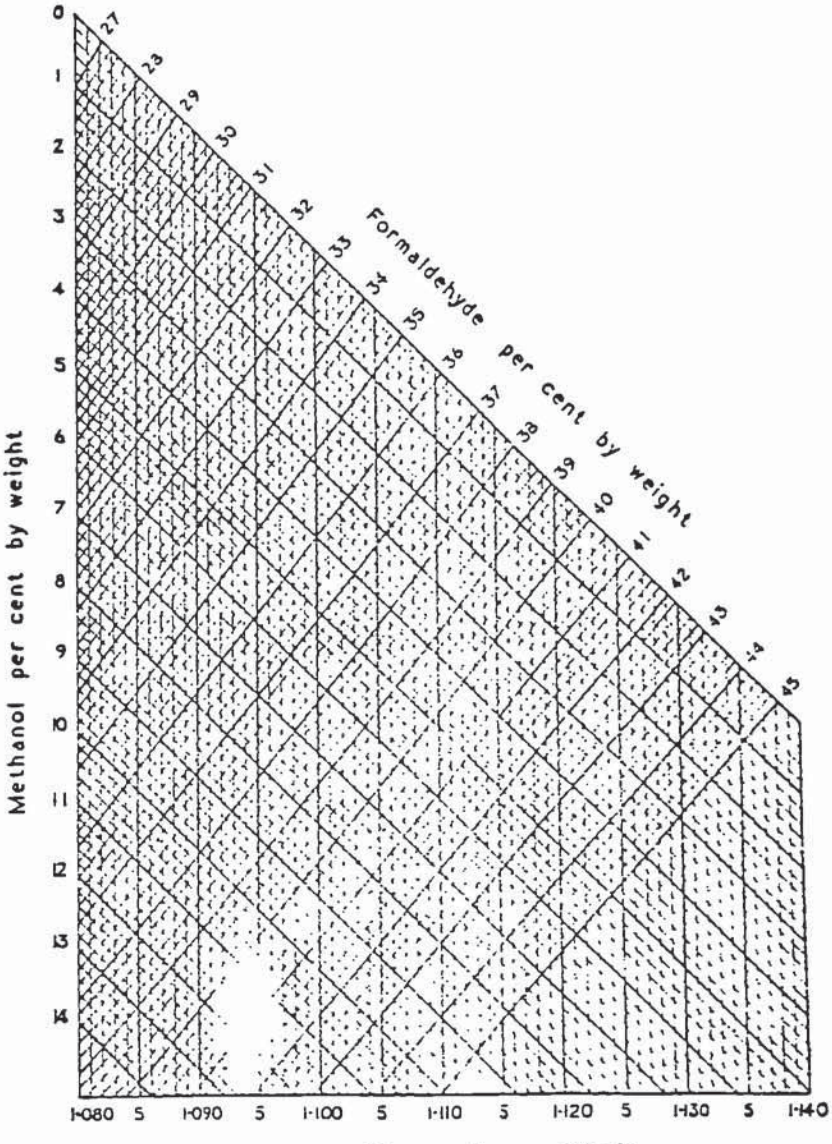


Figure A 3.1 Relationship between Specific Gravity at 25 / 25 °C and Composition of Formaldehyde Solutions.
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A3.4 Oven Solids Contents

A clean tinplate dish, 7 cm in diameter and 1 cm deep, is dried for at least 30 minutes in an oven at 120 °C and after cooling in a desiccator, is weighed to the nearest milligram (W1). 2.0 g ± 0.1 g of the resin sample are weighed into the dish and the sample weight recorded to the nearest milligram (W2). 2.0 mls of xylene (BS458-1) 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 plus contents are placed on a perforated sheet metal shelf and put into an oven which is maintained at a temperature of 120 °C ± 2 °C throughout the determination. After two hours, the dish is removed from the oven, allowed to cool in a desiccator and reweighed (W3). The test result is then calculated from the following equation :

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

The test is performed in duplicate and the average result recorded.

A3.5 Vacuum Solids Content

A clean weighing bottle (60 mm diameter and 30 mm depth) with its lid on and both labled, is weighed accurately and the weight is recorded to the nearest one tenth of a milligram (W1). About 0.2 to 0.30 g of the resin mixture sample is taken into the weighing bottle and the lid is replaced immediately and air tightly. The sample bottle with its lid on is weighed accurately and the weight is recorded to the nearest one tenth of a milligram (W2). The sample bottle is moved to spread the sample uniformly over the bottom area of the bottle.

Two watch glasses, one filled with the phosphorous pentoxide powder and the other with the dry charcoal are placed in a vacuum desiccator. A porcelain plate provided with a number of holes in it, is placed in a desiccator to create separate compartment for the sample bottles. The sample bottle is placed on this porcelain plate with its lid open. The desiccator is sealed and vacuum applied. When steady vacuum is reached, a valve on the desiccator is shut and the sample is kept under vacuum. The charcoal absorbs moisture and the phosphorous pentoxide absorbs solvents from the sample. The phosphorous pentoxide powder becomes pink or brown. They need to be replaced at the interval of two or three days, with dry charcoal and fresh phosporous pentoxide powder.

Vacuum is broke through a sulphuric acid seal to ensure that the air entering the desiccator is free of moisture. The desiccator lid is removed and immediately the sample bottle lid is placed air tightly. The sample bottle is weighed accurately and the weight is recorded. The sample bottle is again kept under vacuum in the desiccator as described earlier. The sample bottle is weighed at the interval of two or three days and when the changes in the weight becomes less than 0.5mg, the test is completed and the weight is recorded W3. The test generally takes two to three weeks. The test result is calculated from the following equation :

$$\text{Wt \% Vacuum Solids} = \frac{W3 - W1}{W2 - W1} \times 100$$

The test is performed in duplicate and the average result is recorded.

A3.6 Karl Fischer's titration method to determine the water content of resin mixture

Calibration

Approximately half fill the beaker of a Karl Fisher's apparatus with dry methanol. Add Fisher reagent to the beaker to excess and mix to give a brown colour. Weigh accurately two to three drops of distilled water by difference from a syringe, and add it to the beaker to excess and mix it (light yellow colour). Let this weight to be 'X' g. Carefully, titrate the mixture with the Fisher's reagent until the yellow colour turns to brown. Let the titre to be 't' ml.

$$\text{Fischer Factor,} \qquad f = \frac{X}{t}$$

Analysis

Add the Fischer reagent to the beaker to excess Fischer and mix it (brown colour). Weigh accurately by difference from a syringe, a sample of resin mixture and add it to the beaker and mix it (yellow colour). Let this weight to be 'Y' g. Carefully titrate the mixture with the Fischer reagent to excess Fischer or until the yellow colour turns to brown. Let the titre to be 'T' ml.

Calculation

$$\text{Wt \% } H_2O = \frac{f \text{ x } T}{Y} \text{ x } 100$$

Perform the test two or three times per sample and take the average result.

A3.7 Gas - Liquid Chromatography (GLC) to analyse AD

In order to analyse AD and wet solvent streams which contain water, n-butanol, iso-butanol, xylenes (xylol), formaldehyde and methanol on the Pye Unicam model 204 GLC machine a Poropak Q column should be used. The following operating conditions should then be used to obtain a good peak resolution:

Thermal conductivity detector = 2 (current setting)
Range = x 1
Attenuation = 2
Detector temperature = 250 °C
Injection temperature = 250 °C
Gas = Helium
Gas flow rate = 30 mls/min
Column inlet pressure 1 = 10.5 psig
Column inlet pressure 2 = 9 psig

The column temperature should be programmed as follows :

Column temperature = 75 °C for 20 minutes
Temperature rise = 6 °C/minute
Final temperature = 220 °C
Hold time = 15 minutes

Make up a solution of 2/3 sample 1/3 isopropanol and inject a 5 µl sample into column 1 pressing the 'run' button on the machine and starting the integrator. The total run time should be about 1 hour after which the columns will have to be cooled back to 75 °C before the next sample can be injected.

The constituents eluted in the following order :

	Time (approx. min.)
Water	6.3
Formaldehyde	13 - 20
Methanol	28.5
Isopropanol	35.4
Butanol (Iso)	42.0
Butanol (n)	43.6
3 x Xylol	56.5 & 59.0 & 62.0

Once the peak areas for the particular components have been printed by the intergrator, then the corresponding compositions were calculated from the following equations :

$$\text{Wt \% Water} = 40.00 \times \frac{\text{Water area}}{\text{iso-Propanol area}}$$

$$\text{Wt \% n-Butanol} = 53.25 \times \frac{\text{n-Butanol area}}{\text{iso-Propanol area}}$$

$$\text{Wt \% iso-Butanol} = 54.70 \times \frac{\text{iso-Butanol area}}{\text{iso-Propanol area}}$$

$$\text{Wt \% Xylol} = 60.00 \times \frac{\text{Xylol area}}{\text{iso-Propanol area}}$$

$$\text{Wt \% Formaldehyde} = 46.21 \times \frac{\text{Formaldehyde area}}{\text{iso-Propanol area}} + 0.9$$

$$\text{Wt \% Methanol} = 100 - [\text{Sum of other components}]$$

APPENDIX 4

EXPERIMENTAL AND ANALYTICAL DETAILS OF LABORATORY AND PLANT SCALE EXPERIMENTS
VP1, 2, 5 - 11, Works 1-2

A4.1 EXPERIMENT VP1

Raw Materials			Density @ 25 °C	Quantity g
Melamine	680	g		680.00
Formalin	1.790	l	1.1253	2014.29
n-Butanol	1.851	l	0.8060	1491.91
Total			0.9720	4186.20

Volume 4186.20/(0.9720 x 1000) = 4.307 l

Formaldehyde (g) 2014.29 x 0.44 = 886.290 g

Formaldehyde (mol/l) 29.51/4.307 = 6.852 mol/l

Table A4.1 Free Formaldehyde Analysis : VP1

Reaction Time min	Reaction Temperature °C	pH	Free Formaldehyde % (wt)	Free Formaldehyde g	Free Formaldehyde mol/l
0	27	7.7		886.29	6.85
10	41		19.35	809.99	6.26
20	77	8.0	9.46	393.91	3.06
30	95		5.71	236.91	1.85
40	95		5.52	228.20	1.79
50	95		5.43	223.66	1.76
60	95	8.0	5.39	221.21	1.74

Molar ratio, Formaldehyde / Melamine = 5.45

A4.2 EXPERIMENT VP2

Raw Materials			Density @ 25 °C	Quantity g
Melamine	680	g		680.00
Formalin	1.730	l	1.1253	1946.77
n-Butanol	1.851	l	0.8060	1491.91
Total			0.9720	4118.68

Volume 4118.68/(0.9720 x 1000) = 4.237 l
Formaldehyde (g) 1946.77 x 0.44 = 856.580 g
Formaldehyde (mol/l) 28.52/4.237 = 6.734 mol/l

Table A4.2 Free Formaldehyde Analysis : VP2

Reaction Time min	Reaction Temperature ℃	pH	Free Formaldehyde % (wt)	Free Formaldehyde g	Free Formaldehyde mol/l
0	28	7.7	20.80	856.54	6.73
10	43		19.31	791.13	6.25
20	77		9.13	372.69	2.96
30	94		5.30	215.76	1.72
40	94	8.0	5.25	213.10	1.70
55	94		5.10	206.40	1.66
70	94		5.00	201.80	1.63

Molar ratio, Formaldehyde/Melamine = 5.25

A4.3 EXPERIMENT VP5

Table A4.3 Raw Materials : VP5

Material		**Density @ 25 °C**	**Quantity g**
Melamine	680.000 g		680.00
Formalin	1.730 l	1.1246	1945.60
n-Butanol (1)	1.851 l	0.8068	1493.40
			4119.00
Xylol	0.264 l	0.8604	227.10
n-Butanol (2)	0.459 l	0.8068	370.32
n-Butanol (3)	0.300 l	0.8068	242.04
n-Butanol (4)	0.050 l	0.8068	40.34

Formalin Compositions	**Wt %**	**Quantity g**
Formaldehyde	43.74	851.01
Water	52.66	1024.55
Methanol	3.60	70.04
		1945.60

Molar Ratio

F : M : B = 5.25 : 1 : 3.74 (28.34 : 5.39 : 20.15)

Table A4.4 Experimental Detail : VP5

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
		4.72				1.851 l n-Butanol charged
		6.12				0.25 ml Caustic added
						680 g Melamine charged
						Methylolation
0	27					Heat on
25	95					Boiling commenced
40	95					Sample 1M 19.1 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
3	93					Boiling Commenced
80	93				380	Sample 1D 24.8 g
160	95		1.9	1.0	868	Sample 2D 27.0 g
						0.459 l n-Butanol added
240	102			2.1	1196	Sample 3D 26.0 g
						Heat off
						Acid Reaction
						3.794 ml Acid catalyst added
0						Heat on
30	103					0.300 l n-Butanol added
60	107		2.4	8.5	1341	Sample 1A 25.0 g
120	116		3.3	16.5	1435	Sample 2A 24.0 g
180	118		4.0	22.5	1464	Sample 3A 25.0 g
200						0.050 l n-Butanol added
230	118		4.2	26.8	1479	Sample 4A 24.2 g
						Heat off, Cooling on.

A4.4 EXPERIMENT VP6

Table A4.5 Raw Materials : VP6

Material			**Density @ 25 °C**	**Quantity g**
Melamine	680.000	g		680.00
Formalin	1.730	l	1.1253	1946.77
n-Butanol (1)	1.851	l	0.8058	1491.54
				4118.31
Xylol	0.264	l	0.8607	227.22
n-Butanol (2)	0.459	l	0.8058	369.86
n-Butanol (3)	0.300	l	0.8058	241.74
n-Butanol (4)	0.100	l	0.8058	80.58

Formalin Compositions	**Wt %**	**Quantity g**
Formaldehyde	43.95	855.60
Water	52.55	1023.03
Methanol	3.50	68.14
		1946.77

Molar Ratio

F : M : B = 5.29 : 1 : 3.74 (28.49 : 5.39 : 20.12)

Table A4.6 Initial Charge : VP6

Material	Quantity g	Composition % (wt)
Melamine	680.00	16.51
n-Butanol	1491.54	36.22
Formaldehyde	855.60	20.78
Water	1023.03	24.84
Methanol	67.14	1.66
Total	4118.31	100.01

Table A4.7 Experimental Detail : VP6

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
	28	4.75				1.851 l n-Butanol charged
		5.97				0.32 ml Caustic added
						680 g Melamine charged
						Methylolation
0	28					Heat on
25	95					Boiling commenced
40	95		0.20			Sample 1M 23.7 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
40	94		0.80		262	Sample 1D 22.6 g
80	94		1.55		471	Sample 2D 20.6 g
160	95		3.35		822	Sample 3D 22.8 g
						0.459 n-Butanol added
240	102		3.50	2.9	1222	Sample 4D 18.4 g
						Heat off
						Acid Reaction
						3.794 ml Acid catalyst added
0						Heat on
40	104		4.70	5.7	1319	Sample 1A 19.3 g
						0.300 l n-Butanol added
80	110		4.00	11.8	1393	Sample 2A 20.2 g
120	116		4.90	16.6	1439	Sample 3A 19.8 g
						0.100 l n-Butanol added
180	122		4.50	25.0	1477	Sample 4A 20.3 g
240	123		5.10	32.8	1496	Sample 5A 21.9 g
						Heat off, Cooling on
						Solvent Adjustment
						Vacuum Equipment Set up
0	18					Vacuum and Heat on
40	55					0.470 l wet solvent off
						Vacuum and Heat off
						Cooling on.

Table A4.8 Materials in the Reactor : VP6

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.84	36.22	1.66	-	20.78	16.51	
		g	1023.03	1491.54	68.14		855.60	680.00	4118.31
1M	40	%	24.84	36.22	1.66	-	5.20	32.05	
		g	1023.03	1491.54	68.14		214.15	1319.92	4118.31
1D	40	%	24.30	21.82	1.29	5.59	4.90	42.10	
		g	987.49	886.71	52.27	227.22	199.12	1710.84	4063.76
3D	160	%	15.30	22.78	0.69	6.48	4.80	49.95	
		g	530.48	789.83	23.84	224.75	166.43	1731.88	3467.22
4D	240	%	5.50	32.84	0.33	6.53	4.20	50.60	
		g	187.97	1122.35	11.38	223.27	143.54	1729.33	3417.64
1A	40	%	4.20	30.54	0.25	6.72	4.15	54.14	
		g	138.72	1008.71	8.33	222.07	137.07	1788.20	3302.91
2A	80	%	2.98	33.68	0.17	6.40	3.82	52.95	
		g	102.86	1162.57	5.71	220.77	131.86	1827.74	3451.82
3A	120	%	2.50	32.50	0.13	6.48	3.79	54.60	
		g	84.65	1100.39	4.31	219.48	123.32	1848.66	3385.83
4A	180	%	1.61	34.07	0.10	6.40	3.67	54.15	
		g	54.88	1161.34	3.33	218.20	125.10	1845.81	3408.70
5A	240	%	1.17	34.16	0.08	6.44	3.65	54.50	
		g	39.42	1151.00	2.84	216.90	122.98	1836.35	3369.45

Table A4.9 Materials in AD : VP6

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	40	%	84.00	4.50	6.00	-	5.50	-	
		g	216.78	11.61	15.48		14.19		258.07
2D	80	%	84.00	4.70	5.80	-	5.50	-	
		g	173.21	9.69	11.96		11.34		206.20
3D	160	%	85.00	4.80	4.60	-	5.60	-	
		g	295.07	16.66	15.97		19.44		347.14
4D	240	%	86.30	4.90	3.10	-	5.70	-	
		g	342.30	19.44	12.30		22.61		396.64
1A	40	%	86.00	5.10	3.10	-	5.80	-	
		g	82.84	4.91	2.99		5.59		96.33
2A	80	%	85.40	5.50	3.10	-	6.00	-	
		g	62.79	4.04	2.57		4.41		73.53
3A	120	%	84.70	6.00	3.00	-	6.30	-	
		g	36.78	2.75	1.37		2.88		45.79
4A	180	%	84.30	6.50	2.50	-	6.70	-	
		g	31.96	2.46	0.95		2.54		37.91
5A	240	%	84.30	6.50	2.50	-	6.70	-	
		g	15.97	1.23	0.47		1.27		18.95

Table A4.10 Materials in Samples : VP6

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	40	g	5.89	6.58	0.39	-	1.23	7.60	23.7
1D	40	g	5.49	4.93	0.29	1.26	1.11	9.51	22.6
2D	80	g	4.68	4.40	0.21	1.21	1.00	9.09	20.6
3D	160	g	3.49	5.19	0.16	1.48	1.09	11.39	22.8
4D	240	g	1.01	5.92	0.06	1.20	0.77	9.31	18.4
1A	40	g	0.81	5.89	0.05	1.30	0.80	10.45	19.3
2A	80	g	0.60	6.80	0.03	1.29	0.77	10.70	20.2
3A	120	g	0.50	6.44	0.03	1.28	0.75	10.81	19.8
4A	180	g	0.33	6.92	0.02	1.30	0.75	10.99	20.3

Table A4.11 Mass Balance for Water : VP6

Sample No.	Time in Process Stage min	Water in the reactor g	Water off with AD g	Water off with sample g	Total g	Water Produced g	Water Produced gmol
1M	40	1023.03					
1D	40	987.49	216.78	5.89	1210.16	187.13	10.39
2D	80		173.21	5.49			
3D	160	530.48	295.07	4.68	1008.93	21.44	1.19
4D	240	187.97	342.30	3.49	533.76	3.28	0.18
1A	40	138.72	82.84	1.01	222.57	34.60	1.92
2A	80	102.86	62.79	0.81	166.46	27.74	1.54
3A	120	84.65	36.78	0.60	122.03	19.17	1.06
4A	180	54.88	31.96	0.50	87.34	2.69	0.15
5A	240	39.42	15.97	0.33	55.72	0.84	0.05

Table A4.12 Mass Balance for n-Butanol : VP6

Sample No.	Time in Process Stage min	Butanol in the reactor g	Butanol off with AD g	Butanol off with sample g	Total g	Butanol Reacted g	Butanol Reacted gmol
1M	40	1491.54					
1D	40	886.71	11.61	6.58	904.90	586.64	7.91
2D	80		9.69	4.93			
3D	160	789.83 (+369.86)	16.35	4.40	825.51	61.20	0.83
4D	240	1122.35	19.44	5.19	1146.98	12.71	0.17
1A	40	1008.71 (+241.74)	4.91	5.92	1019.54	102.81	1.39
2A	80	1162.57	4.04	5.89	1172.50	77.95	1.05
3A	120	1100.39 (+80.58)	2.75	6.80	1109.94	52.63	0.71
4A	180	1161.34	2.46	6.44	1170.24	10.73	0.14
5A	240	1151.00	1.23	6.92	1159.15	2.19	0.03

Table A4.13 Mass Balance for Solids : VP6

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
1M	40	1319.92	-	-	1319.92	639.92
1D	40	1710.84	-	7.60	1718.44	398.52
2D	80			9.51		
3D	160	1731.88	-	9.09	1750.48	39.64
4D	240	1729.33	-	11.39	1740.72	8.84
1A	40	1788.20	-	9.31	1797.51	68.18
2A	80	1827.74	-	10.45	1838.19	49.99
3A	120	1848.66	-	10.70	1859.36	31.62
4A	180	1845.81	-	10.81	1856.62	7.96
5A	240	1836.35	-	10.99	1847.34	1.53

A4.5 EXPERIMENT VP7

Table A4.14 Raw Materials : VP7

Material		**Density @ 25 °C**	**Quantity g**
Melamine	680.000 g		680.00
Formalin	1.730 l	1.1258	1947.63
n-Butanol (1)	2.129 l	0.8058	1715.55
			4343.18
Xylol	0.264 l	0.8609	227.28
n-Butanol (2)	0.459 l	0.8058	369.86
Formalin Compositions		**Wt %**	**Quantity g**
Formaldehyde		44.15	859.88
Water		52.35	1019.58
Methanol		3.50	68.17
			1947.63

Molar Ratio

F : M : B = 5.31 : 1 : 4.30 (28.63 : 5.39 : 23.15)

Table A4.15 Initial Charge : VP7

Material	Quantity g	Composition % (wt)
Melamine	680.00	15.66
n-Butanol	1715.55	39.50
Formaldehyde	859.88	19.80
Water	1019.58	23.48
Methanol	68.17	1.57
Total	4343.18	100.01

Table A4.16 Experimental Detail : VP7

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
		4.64				2.129 l n-Butanol charged
	29	6.14				0.46 ml Caustic added
						680 g Melamine charged
						Methylolation
0	29					Heat on
25	94					Boiling commenced
40	94					Sample 1M 15.9 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
40	93		0.40		215	Sample 1D 15.9 g
80	93		0.80		436	Sample 2D 18.7 g
160	95		1.55		971	Sample 3D 23.6 g
215	102		1.55		1231	Sample 4D 31.9 g
						Heat off, Cooling on.

Table A4.17 Materials in the Reactor : VP7

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	23.48	39.50	1.57	-	19.80	15.66	
		g	1019.58	1715.55	68.17		859.88	680.00	4343.18
1M	40	%	23.48	39.50	1.57	-	4.91	30.62	
		g	1019.58	1715.55	68.17		213.25	1329.88	4343.18
1D	40	%	22.66	27.21	1.29	5.23	4.62	38.99	
		g	984.02	1181.61	55.84	227.28	200.63	1693.16	4342.55
2D	80	%	20.70	25.40	1.06	5.51	4.60	42.73	
		g	850.51	1043.62	43.44	226.45	189.00	1755.66	4108.74
3D	160	%	11.35	26.97	0.55	6.33	4.65	50.15	
		g	404.16	960.37	19.43	225.42	165.58	1785.78	3560.87
4D	215	%	4.90	35.75	0.29	6.14	4.22	48.70	
		g	178.82	1304.67	10.54	223.93	154.01	1777.28	3649.44

Table A4.18 Materials in AD : VP7

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	40	%	84.50	4.50	5.70	-	5.30	-	
		g	179.15	9.54	12.08		11.24		212.01
2D	80	%	85.00	4.70	5.60	-	4.70	-	
		g	185.22	10.24	12.20		10.24		217.91
3D	160	%	86.20	5.00	4.50	-	4.30	-	
		g	456.14	26.46	23.81		22.75		529.17
4D	215	%	87.00	5.50	3.40	-	4.10	-	
		g	224.19	14.17	8.76		10.57		257.69

Table A4.19 Materials in Samples : VP7

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	40	g	3.73	6.28	0.25	-	0.78	4.87	15.9
1D	40	g	3.60	4.33	0.20	0.83	0.73	6.20	15.9
2D	80	g	3.87	4.75	0.20	1.03	0.86	7.99	18.7
3D	160	g	2.68	6.36	0.13	1.49	1.10	11.84	23.6

Table A4.20 Mass Balance for Water : VP7

Sample No.	Time in Process Stage min	Water in the reactor g	Water off with AD g	Water off with sample g	Total g	Water Produced g	gmol
1M	40	1019.18					
1D	40	984.02	179.15	3.73	1166.90	147.32	8.18
2D	80	850.51	185.22	3.60	1039.33	55.31	3.07
3D	160	404.16	456.14	3.87	864.17	13.66	0.76
4D	215	178.82	224.19	2.68	405.69	1.53	0.08

Table A4.21 Mass Balance for n-Butanol : VP7

Sample No.	Time in Process Stage min	Butanol in the reactor g	Butanol off with AD g	Butanol off with sample g	Total g	Butanol Reacted g	gmol
1M	40	1715.55					
1D	40	1181.61	9.54	6.28	1197.43	518.12	6.99
2D	80	1043.62	10.24	4.33	1058.19	123.42	1.67
3D	160	960.37	26.46	4.75	991.58	52.04	0.70
		(+369.86)					
4D	215	1304.67	14.17	6.36	1325.20	5.03	0.07

Table A4.22 Mass Balance for Solids : VP7

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
1M	40	1329.88	-	-	1329.88	649.88
1D	40	1693.16	-	4.87	1698.03	367.77
2D	80	1755.66		6.20	1761.86	67.73
3D	160	1785.78	-	7.99	1792.99	40.27
4D	215	1777.28	-	11.84	1789.12	4.11

A4.6 EXPERIMENT VP8

Table A4.23 Raw Materials : VP8

Material			**Density @ 25 °C**	**Quantity g**
Melamine	680.000	g		680.00
Formalin	1.730	l	1.1254	1947.63
n-Butanol (1)	1.666	l	0.8058	1342.46
				3970.09
Xylol	0.264	l	0.8612	227.36
n-Butanol (2)	0.459	l	0.8058	369.86
Formalin Compositions			**Wt %**	**Quantity g**
Formaldehyde			44.05	857.93
Water			52.45	1021.53
Methanol			3.50	68.17
				1947.63

Molar Ratio

F : M : B = 5.30 : 1 : 3.36 (28.57 : 5.39 : 18.11)

Table A4.24 Initial Charge : VP8

Material	Quantity g	Composition % (wt)
Melamine	680.00	17.13
n-Butanol	1342.46	33.81
Formaldehyde	857.93	21.61
Water	1021.53	25.73
Methanol	68.17	1.72
Total	3970.09	100.00

Table A4.25 Experimental Detail : VP8

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
		4.60				1.6661 n-Butanol charged
		6.00				0.50 ml Caustic added
		5.46				0.03 ml Formic acid added
		6.12				0.12 ml Caustic added
						680 g Melamine charged
						Methylolation
0	29					Heat on
25	94					Boiling commenced
40	94					Sample 1M 17.9 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
40	93		0.30		188	Sample 1D 23.5 g
80	93		0.70		378	Sample 2D 23.5 g
160	94		2.30		872	Sample 3D 23.2 g
240	102		4.10		1226	Sample 4D 29.2 g
						Heat off, Cooling on.

Table A4.26 Materials in the Reactor : VP8

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	25.73	33.81	1.72	-	21.61	17.13	
		g	1021.53	1342.46	68.17		857.93	680.00	3970.09
1M	40	%	25.73	33.81	1.72	-	5.40	33.34	
		g	1021.53	1342.46	68.17		214.38	1323.63	3970.09
1D	40	%	25.15	19.98	1.42	5.69	5.10	42.66	
		g	1004.69	798.16	56.77	227.36	203.73	1704.18	3994.80
2D	80	%	23.50	18.51	1.22	5.97	5.10	45.70	
		g	889.31	700.47	46.15	226.02	193.00	1729.42	3784.28
3D	160	%	14.77	19.18	0.68	6.87	5.20	53.30	
		g	483.30	627.60	22.41	224.62	170.15	1744.06	3272.16
4D	240	%	5.41	29.71	0.34	6.83	4.67	53.04	
		g	176.78	970.81	11.01	223.03	152.60	1733.15	3267.62

Table A4.27 Materials in AD : VP8

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	40	%	83.50	5.00	6.00	-	5.50	-	
		g	154.27	9.24	11.09		10.06		184.75
2D	80	%	84.00	5.10	5.50	-	5.40	-	
		g	157.10	9.54	10.29		10.10		187.02
3D	160	%	85.50	5.20	4.80	-	4.50	-	
		g	417.77	25.41	23.45		21.99		488.62
4D	240	%	86.60	5.50	3.20	-	4.70	-	
		g	304.14	19.32	11.24		16.51		351.20

Table A4.28 Materials in Samples : VP8

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	40	g	4.61	6.05	0.31	-	0.97	5.97	17.9
1D	40	g	5.91	4.70	0.33	1.34	1.20	10.03	23.5
2D	80	g	5.52	4.35	0.29	1.40	1.20	10.74	23.5
3D	160	g	3.43	4.45	0.16	1.59	1.21	12.37	23.2

Table A4.29 Mass Balance for Water : VP8

Sample No.	Time in Process Stage	Water in the reactor	Water off with AD	Water off with sample	Total	Water Produced	
	min	g	g	g	g	g	gmol
1M	40	1021.53					
1D	40	1004.69	154.27	4.61	1163.57	142.04	7.88
2D	80	889.31	157.10	5.91	1052.32	47.63	2.64
3D	160	483.30	417.77	5.52	906.59	17.28	0.96
4D	240	176.78	304.14	3.43	484.35	1.05	0.06

Table A4.30 Mass Balance for n-Butanol : VP8

Sample No.	Time in Process Stage min	Butanol in the reactor g	Butanol off with AD g	Butanol off with sample g	Total g	Butanol Reacted g	Butanol Reacted gmol
1M	40	1342.46					
1D	40	798.16	9.24	6.05	813.45	529.01	7.14
2D	80	700.47	9.54	4.70	714.71	83.45	1.13
3D	160	627.60 (+369.86)	25.41	4.35	657.36	43.11	0.58
4D	240	970.81	19.32	4.45	999.16	2.88	0.04

Table A4.31 Mass Balance for Solids : VP8

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
1M	40	1323.63	-	-	1323.63	643.63
1D	40	1704.18	-	5.97	1710.15	386.52
2D	80	1729.42		10.03	1739.45	35.27
3D	160	1744.06	-	10.74	1754.80	25.38
4D	240	1733.15	-	12.37	1745.52	1.46

A4.7 EXPERIMENT VP9

Table A4.32 Raw Materials : VP9

Material		**Density @ 25 °C**	**Quantity g**
Melamine	680.000 g		680.00
Formalin	1.730 l	1.1253	1946.77
n-Butanol (1)	1.851 l	0.8062	1492.28
			4119.05
Xylol	0.264 l	0.8616	227.46
Formalin Compositions		**Wt %**	**Quantity g**
Formaldehyde		43.96	855.80
Water		52.54	1022.83
Methanol		3.60	68.14
			1946.77
Molar Ratio			
F : M : B = 5.29 : 1 : 3.73		(28.50 : 5.39 : 20.13)	

Table A4.33 Initial Charge : VP9

Material	Quantity g	Composition % (wt)
Melamine	680.00	16.51
n-Butanol	1492.28	36.23
Formaldehyde	855.80	20.78
Water	1022.83	24.83
Methanol	68.14	1.65
Total	4119.05	100.00

Table A4.34 Experimental Detail : VP9

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
		4.79				1.851 l n-Butanol charged
	29	7.10				0.30 ml Caustic added
						680 g Melamine charged
						Methylolation
0	29					Heat on
25	94					Boiling commenced
40	94					Sample 1M 14.0 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
15	93				45	Sample 1D 19.3 g
30	93				113	Sample 2D 21.3 g
45	93				181	Sample 3D 21.3 g
60	93				240	Sample 4D 20.0 g
90	94		0.30		394	Sample 5D 21.8 g
120	94		0.35		539	Sample 6D 44.5 g
						Heat off, Cooling on.

Table A4.35 Sampling Details : VP9

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	1M	40 End of Methylolation	14.0	4119.05	-
Dehydration	1D	15	19.3	4287.99	44.52
	2D	30	21.3	4202.12	66.57
	3D	45	21.3	4114.25	66.57
	4D	60	20.0	4035.08	57.87
	5D	90	21.8	3863.74	151.34
	6D	120	44.5	3699.00	142.94

Table A4.36 Materials in the Reactor : VP9

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.83	36.23	1.65	-	20.78	16.51	
		g	1022.83	1492.28	68.14		855.80	680.00	4119.05
1M	40	%	24.83	36.23	1.65	-	5.11	32.18	
		g	1022.83	1492.28	68.14		210.48	1325.51	4119.05
1D	15	%	23.80	31.77	1.57	5.30	4.88	32.68	
		g	1020.54	1362.29	67.15	227.46	209.25	1401.32	4287.99
2D	30	%	23.80	29.17	1.48	5.39	4.88	35.28	
		g	1000.10	1225.76	62.32	226.44	205.06	1482.51	4202.12
3D	45	%	23.30	28.38	1.40	5.48	4.87	36.57	
		g	958.62	1167.62	57.54	225.29	200.36	1504.58	4114.25
4D	60	%	22.84	27.53	1.32	5.55	4.86	37.90	
		g	921.61	1110.86	53.36	224.12	196.10	1529.30	4035.08
5D	90	%	21.25	26.09	1.16	5.77	4.83	40.90	
		g	821.04	1008.05	44.93	223.01	186.62	1580.27	3863.74
6D	120	%	18.88	26.75	1.03	5.99	4.80	42.55	
		g	698.37	989.48	37.96	221.75	177.55	1573.92	3699.00

Table A4.37 Materials in AD : VP9

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	15	%	95.00	2.10	1.70	-	1.20	-	
		g	42.29	0.93	0.76		0.53		44.52
2D	30	%	82.70	5.50	6.80	-	5.00	-	
		g	55.05	3.66	4.53		3.33		66.57
3D	45	%	82.70	5.30	6.70	-	5.30	-	
		g	55.05	3.53	4.46		3.53		66.57
4D	60	%	82.70	5.30	6.70	-	5.30	-	
		g	47.86	3.07	3.88		3.07		57.87
5D	90	%	84.00	5.10	5.40	-	5.50	-	
		g	127.13	7.72	8.17		8.32		151.34
6D	120	%	84.70	5.10	4.70	-	5.50	-	
		g	121.07	7.29	6.72		7.86		142.94

Table A4.38 Materials in Samples : VP9

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	40	g	3.48	5.07	0.23	-	7.15	4.51	14.0
1D	15	g	4.59	6.13	0.30	1.02	0.94	6.31	19.3
2D	30	g	5.07	6.21	0.32	1.15	1.04	7.51	21.3
3D	45	g	4.96	6.04	0.30	1.17	1.07	7.79	21.3
4D	60	g	4.57	5.51	0.26	1.11	0.97	7.58	20.0
5D	90	g	4.63	5.69	0.25	1.26	1.05	8.92	21.8

Table A4.39 Mass Balance for Water : VP9

Sample No.	Time in Process Stage	Water in the reactor	Water off with AD	Water off with sample	Total	Water Produced	
	min	g	g	g	g	g	gmol
1M	40	1022.83					
1D	15	1020.54	42.29	3.48	1066.31	43.48	2.41
2D	30	1000.10	55.05	4.59	1059.74	39.20	2.18
3D	45	958.62	55.05	5.07	1018.74	18.64	1.03
4D	60	921.61	47.86	4.96	974.43	15.81	0.88
5D	90	821.04	127.13	4.57	952.74	31.13	1.73
6D	120	698.37	121.07	4.63	824.07	3.03	0.17

Table A4.40 Mass Balance for n-Butanol : VP9

Sample No.	Time in Process Stage	Butanol in the reactor	Butanol off with AD	Butanol off with sample	Total	Butanol Reacted	
	min	g	g	g	g	g	gmol
1M	40	1492.28					
1D	15	1362.29	0.93	5.07	1368.29	123.99	1.67
2D	30	1225.76	3.66	6.13	1235.55	126.74	1.71
3D	45	1167.62	3.53	6.21	1177.36	48.40	0.65
4D	60	1110.86	3.07	6.04	1119.97	47.65	0.64
5D	90	1008.05	7.72	5.51	1021.28	89.58	1.21
6D	120	989.48	7.29	5.69	1002.46	5.59	0.08

Table A4.41 Mass Balance for Solids : VP9

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
1M	40	1325.51	-	-	1325.51	645.51
1D	15	1401.32	-	4.51	1405.83	80.32
2D	30	1482.51		6.31	1488.82	87.50
3D	45	1504.58	-	7.51	1512.09	29.58
4D	60	1529.30	-	7.79	1537.09	32.51
5D	90	1580.27	-	7.58	1587.85	58.55
6D	120	1573.92	-	8.92	1582.84	2.57

Table A4.42 Results of the mass balances : VP9

Process Stage	Sample No.	Differential Time Δt min	Water Produced		n-Butanol Reacted		Solids Increase
			g	gmol	g	gmol	g
Methylolation	1M	40	-	-	-	-	645.51
Dehydration	1D	15	43.48	2.41	123.99	1.67	80.32
	2D	15	39.20	2.18	126.74	1.71	87.50
	3D	15	18.64	1.03	48.40	0.65	29.58
	4D	15	15.81	0.88	47.65	0.64	32.51
	5D	30	31.13	1.73	89.58	1.21	58.55
	6D	30	3.03	0.17	5.59	0.08	2.57

Table A4.43 Chemical changes over a differential reaction time : VP9

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Dehydration	1D	15	1.67	0.74	3.15
	2D	15	1.71	0.47	2.65
	3D	15	0.65	0.38	1.41
	4D	15	0.64	0.24	1.12
	5D	30	1.21	0.52	2.25
	6D	30	0.08	0.09	0.26

Table A4.44 Experimental and Theoretical Solids : VP9

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Dehydration	1D	15	80.32	80.36
	2D	15	87.50	87.47
	3D	15	29.58	29.62
	4D	15	32.51	31.58
	5D	30	58.55	58.52
	6D	30	2.57	2.87

Table A4.45 Chemical changes as a function of time : VP9

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
					21.49
Dehydration	1D	15	0.74	1.67	18.34
	2D	30	1.21	3.38	15.69
	3D	45	1.59	4.03	14.28
	4D	60	1.83	4.67	13.16
	5D	90	2.35	5.88	10.91
	6D	120	2.44	5.96	10.65

A4.8 EXPERIMENT VP10

Table A4.46 Raw Materials : VP10

Material		**Density @ 25 °C**	**Quantity g**
Melamine	680.000 g		680.00
Formalin	1.730 l	1.1253	1946.77
n-Butanol (1)	1.851 l	0.8062	1492.28
			4119.05
Xylol	0.264 l	0.8616	227.46
Formalin Compositions		**Wt %**	**Quantity g**
Formaldehyde		43.96	855.80
Water		52.54	1022.83
Methanol		3.50	68.14
			1946.77
Molar Ratio			
F : M : B = 5.29 : 1 : 3.73		(28.50 : 5.39 : 20.13)	

Table A4.47 Initial Charge : VP10

Material	Quantity g	Composition % (wt)
Melamine	680.00	16.51
n-Butanol	1492.28	36.23
Formaldehyde	855.80	20.78
Water	1022.83	24.83
Methanol	68.14	1.65
Total	4119.05	100.00

Table A4.48 Experimental Detail : VP10

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
		4.79				1.851 l n-Butanol charged
		5.47				0.12 ml Caustic added
						680 g Melamine charged
						Methylolation
0	29					Heat on
25	94					Boiling commenced
40	94					Sample 1M 24.0 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
15	93				66	Sample 1D 21.5 g
30	93				115	Sample 2D 22.1 g
45	93				179	Sample 3D 21.7 g
60	93		0.20+		240	Sample 4D 21.4 g
80	93		0.27		312	Sample 5D 21.3 g
120	94		0.50-		534	Sample 6D 50.1 g
						Heat off, Cooling on.

Table A4.49 Sampling Details : VP10

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	1M	40 End of Methylolation	24.0	4119.05	-
Dehydration	1D	15	21.5	4257.65	64.86
	2D	30	22.1	4188.15	48.00
	3D	45	21.7	4103.27	62.78
	4D	60	21.4	4021.66	59.91
	5D	80	21.3	3929.46	70.80
	6D	120	50.1	3689.31	218.85

Table A4.50 Materials in the Reactor : VP10

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.83	36.23	1.65	-	20.78	16.51	
		g	1022.83	1492.28	68.14		855.80	680.00	4119.05
1M	40	%	26.20	32.07	1.65	-	5.08	35.00	
		g	1079.19	1320.98	68.14		209.25	1441.67	4119.05
1D	15	%	25.30	27.15	1.51	5.34	4.81	35.89	
		g	1077.19	1155.95	64.11	227.46	204.81	1528.07	4257.65
2D	30	%	25.40	25.24	1.45	5.40	4.81	37.70	
		g	1063.79	1057.09	60.57	226.31	201.45	1578.93	4188.15
3D	45	%	25.15	24.39	1.37	5.49	4.80	38.80	
		g	1031.97	1000.79	56.29	225.12	196.96	1592.07	4103.27
4D	60	%	24.47	24.16	1.30	5.57	4.80	39.70	
		g	984.10	971.63	52.46	223.93	192.64	1596.60	4021.66
5D	80	%	23.45	24.42	1.23	5.67	4.78	40.45	
		g	921.46	959.57	48.36	222.74	187.83	1589.47	3929.46
6D	120	%	19.83	25.55	1.02	6.00	4.75	42.85	
		g	731.59	942.62	37.81	221.53	175.24	1580.87	3689.31

Table A4.51 Materials in AD : VP10

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	15	%	83.70	5.40	5.60	-	5.30	-	
		g	54.29	3.50	3.63		3.44		64.86
2D	30	%	82.90	5.40	6.70	-	5.00	-	
		g	39.80	2.59	3.22		2.40		48.00
3D	45	%	82.70	5.60	6.30	-	5.40	-	
		g	51.92	3.52	3.96		3.39		62.78
4D	60	%	83.10	5.60	5.90	-	5.40	-	
		g	49.79	3.35	3.53		3.24		59.91
5D	80	%	83.70	5.40	5.40	-	5.50	-	
		g	59.26	3.82	3.82		3.89		70.80
6D	120	%	84.50	5.30	4.70	-	5.50	-	
		g	184.93	11.60	10.29		12.04		218.85

Table A4.52 Materials in Samples : VP10

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	40	g	6.29	7.70	0.40	-	1.22	8.40	24.0
1D	15	g	5.44	5.84	0.32	1.15	1.03	7.72	21.5
2D	30	g	5.61	5.58	0.32	1.19	1.06	8.33	22.1
3D	45	g	5.46	5.29	0.30	1.19	1.04	8.42	21.7
4D	60	g	5.24	5.17	0.28	1.19	1.02	8.50	21.4
5D	80	g	4.99	5.20	0.26	1.21	1.02	8.62	21.3

Table A4.53 Mass Balance for Water : VP10

Sample No.	Time in Process Stage	Water in the reactor	Water off with AD	Water off with sample	Total	Water Produced	
	min	g	g	g	g	g	gmol
0	0	1022.83					
1M	40	1079.19	-	-	1079.19	56.36	3.13
1D	15	1077.19	54.29	6.29	1137.77	58.58	3.25
2D	30	1063.79	39.80	5.44	1109.03	31.84	1.77
3D	45	1031.97	51.92	5.61	1089.50	25.71	1.43
4D	60	984.10	49.79	5.46	1039.35	7.38	0.41
5D	80	921.46	59.26	5.24	985.96	1.86	0.10
6D	120	731.59	184.93	4.99	921.51	0.05	0.00

Table A4.54 Mass Balance for n-Butanol : VP10

Sample No.	Time in Process Stage	Butanol in the reactor	Butanol off with AD	Butanol off with sample	Total	Butanol Reacted	
	min	g	g	g	g	g	gmol
0	0	1492.28					
1M	40	1320.98	-	-	1320.98	171.30	2.31
1D	15	1155.95	3.50	7.70	1167.15	153.83	2.08
2D	30	1057.09	2.59	5.84	1065.52	90.43	1.22
3D	45	1000.79	3.52	5.58	1009.89	47.20	0.64
4D	60	971.63	3.35	5.29	980.27	20.52	0.28
5D	80	959.57	3.82	5.17	968.56	3.07	0.04
6D	120	942.62	11.60	5.20	959.42	0.15	0.00

Table A4.55 Mass Balance for Solids : VP10

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
1M	40	1441.67	-	-	1441.67	646.55* 115.12
1D	15	1528.07	-	8.40	1536.47	94.80
2D	30	1578.93		7.72	1586.65	58.58
3D	45	1592.07	-	8.33	1600.40	21.47
4D	60	1596.60	-	8.42	1605.02	12.95
5D	80	1589.47	-	8.50	1597.97	1.37
6D	120	1580.87	-	8.62	1589.49	0.02

* Solids increase due to methylolation

Table A4.56 Results of the mass balances : VP10

Process Stage	Sample No.	Differential Time Δt min	Water Produced		n-Butanol Reacted		Solids Increase
			g	gmol	g	gmol	g
Methylolation	1M	40	56.36	3.13	171.30	2.31	646.55* 115.12
Dehydration	1D	15	58.58	3.25	153.83	2.08	94.80
	2D	15	31.84	1.77	90.43	1.22	58.58
	3D	15	25.71	1.43	47.20	0.64	21.47
	4D	15	7.38	0.41	20.52	0.28	12.95
	5D	20	1.86	0.10	3.07	0.04	1.37
	6D	40	0.05	0.00	0.15	0.00	0.02

* Solids increase due to methylolation

Table A4.57 Chemical changes over a differential reaction time : VP10

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Methylolation	1M		2.31	0.82	3.95
Dehydration	1D	15	2.08	1.17	4.42
	2D	15	1.22	0.55	2.32
	3D	15	0.64	0.79	2.22
	4D	15	0.28	0.13	0.54
	5D	20	0.04	0.06	0.16
	6D	40	0.00	0.00	0.00

Table A4.58 Experimental and Theoretical Solids : VP10

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Methylolation	1M		115.12	114.83
Dehydration	1D	15	94.80	95.62
	2D	15	58.58	58.54
	3D	15	21.47	21.68
	4D	15	12.95	13.37
	5D	20	1.37	1.16
	6D	40	0.02	0.00

Table A4.59 Chemical changes as a function of time : VP10

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
					21.53
Methylolation	1M	40	0.82	2.31	17.58
Dehydration	1D	15	1.99	4.39	13.16
	2D	30	2.54	5.61	10.84
	3D	45	3.33	6.25	8.22
	4D	60	3.46	6.53	8.08
	5D	80	3.52	6.57	7.92
	6D	120	3.52	6.57	7.92

A4.9 EXPERIMENT VP11

Table A4.60 Raw Materials : VP11

Material		**Density @ 25 °C**	**Quantity g**
Melamine	680.000 g		680.00
Formalin	1.730 l	1.1253	1946.77
n-Butanol (1)	1.851 l	0.8062	1492.28
			4119.05
Xylol	0.264 l	0.8616	227.46
n-Butanol (2)	0.459 l	0.8062	370.05
Formalin Compositions		**Wt %**	**Quantity g**
Formaldehyde		43.96	855.80
Water		52.54	1022.83
Methanol		3.50	68.14
			1946.77

Initial Molar Ratio

F : M : B = 5.29 : 1 : 3.73 (28.50 : 5.39 : 20.13)

Table A4.61 Initial Charge : VP11

Material	Quantity g	Composition % (wt)
Melamine	680.00	16.51
n-Butanol	1492.28	36.23
Formaldehyde	855.80	20.78
Water	1022.83	24.83
Methanol	68.14	1.65
Total	4119.05	100.00

Table A4.62 Experimental Detail : VP11

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off ml	Comments
						Charge Preparation
						1.73 l Formalin charged
		4.62				1.851 l n-Butanol charged
	28	5.89				0.27 ml Caustic added
						680 g Melamine charged
						Methylolation
0	28					Heat on
22	83					Sample M0 5.0 g
25	94					Boiling commenced
40	94					Sample 1M 19.3 g
						Heat off
						Dehydration
						0.264 l Xylol charged
						Overhead Equip. changed
0						Heat on
15	92				43	Sample 1D 20.7 g
30	92				97	Sample 2D 20.8 g
45	92				144	Sample 3D 20.4 g
60	93		0.20		199	Sample 4D 20.1 g
90	93		0.30-		360	Sample 5D 21.9 g
120	94		0.40-		528	Sample 6D 30.5 g
						Heat off
						Extended Dehydration
						0.459 l n-Butanol added
1350	103		5.40		1243	Sample 7D 22.2 g
3066	121		10.00+		1434	Sample 8D 44.2 g
4248	122				1456	Sample 9D 27.0 g
						Heat off, Cooling on.

Table A4.63 Sampling Details : VP11

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample g	Wt. of Resin in Reactor including sample g	Wt. of AD removed g
Methylolation	M0	22	5.0	4119.05	-
	1M	40	19.3	4114.05	-
		End of Methylolation			
Dehydration	1D	15	20.7	4279.64	42.57
	2D	30	20.8	4206.09	52.85
	3D	45	20.4	4139.27	46.02
	4D	60	20.1	4064.94	53.93
	5D	90	21.9	3886.50	158.34
	6D	120	30.5	3698.87	165.73
	7D	1350	22.2	3330.86	707.56
	8D	3066	44.2	3117.35	191.31
	9D	4248		3050.99	22.16

Table A4.64 Materials in the Reactor : VP11

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.83	36.23	1.65	-	20.78	16.51	
		g	1022.83	1492.28	68.14		855.80	680.00	4119.05
M0	22	%	24.83	36.23	1.65	-	7.51	29.80	
		g	1022.83	1492.28	68.14		309.34	1227.48	4119.05
1M	40	%	25.25	35.00	1.65	-	5.10	33.00	
		g	1038.80	1439.92	68.06		209.80	1357.64	4114.05
1D	15	%	24.40	29.86	1.56	5.31	4.87	34.00	
		g	1044.23	1277.90	66.93	227.46	208.42	1455.08	4279.64
2D	30	%	24.60	27.77	1.50	5.38	4.86	35.89	
		g	1034.70	1168.03	63.02	226.36	204.41	1509.57	4206.09
3D	45	%	24.54	26.74	1.44	5.44	4.85	36.99	
		g	1015.78	1106.84	59.58	225.24	200.75	1531.11	4139.27
4D	60	%	24.35	24.93	1.37	5.51	4.84	39.00	
		g	989,81	1013.39	55.84	224.13	196.74	1585.33	4064.94
5D	90	%	22.40	24.19	1.21	5.74	4.76	41.70	
		g	870.58	940.14	47.01	223.02	185.00	1620.67	3886.50
6D	120	%	19.63	24.99	1.05	6.00	4.73	43.60	
		g	726.09	924.35	38.80	221.76	174.96	1612.71	3698.87
7D	1350	%	4.60	33.77	0.75	6.60	3.98	50.30	
		g	153.22	1124.83	25.04	219.93	132.57	1675.42	3330.86
8D	3066	%	0.68	30.92	0.77	7.01	3.75	56.87	
		g	21.20	963.88	23.91	218.46	116.90	1772.84	3117.35
9D	4248	%	0.52	29.36	0.75	7.06	3.71	58.60	
		g	15.87	895.77	22.77	215.36	113.19	1787.88	3050.99

Table A4.65 Materials in AD : VP11

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	15	%	95.00	2.10	1.90	-	1.00	-	
		g	40.44	0.89	0.81		0.43		42.57
2D	30	%	82.90	5.30	6.80	-	5.00	-	
		g	43.81	2.80	3.59		2.64		52.85
3D	45	%	82.80	5.00	6.80	-	5.40	-	
		g	38.10	2.30	3.13		2.49		46.02
4D	60	%	82.70	5.40	6.40	-	5.50	-	
		g	44.60	2.91	3.45		2.97		53.93
5D	90	%	83.60	5.50	5.40	-	5.50	-	
		g	132.37	8.71	8.55		8.71		158.34
6D	120	%	84.50	5.20	4.80	-	5.50	-	
		g	140.04	8.62	7.95		9.12		165.73
7D	1350	%	87.00	5.30	1.90	-	5.80	-	
		g	615.58	37.50	13.44		41.04		707.56
8D	3066	%	87.00	5.00	0.50	-	7.50	-	
		g	166.44	9.57	0.96		14.35		191.31
9D	4248	%	82.20	4.80	3.60	-	9.40	-	
		g	18.22	1.06	0.80		2.08		22.16

Table A4.66 Materials in Samples : VP11

Sample No.	Time in Process Stage min	% or g	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
M0	22	g	1.24	1.81	0.08	-	0.38	1.49	5.0
1M	40	g	4.87	6.76	0.32	-	0.98	6.37	19.3
1D	15	g	5.05	6.18	0.32	1.10	1.01	7.04	20.7
2D	30	g	5.12	5.78	0.31	1.12	1.01	7.47	20.8
3D	45	g	5.01	5.45	0.29	1.11	0.99	7.55	20.4
4D	60	g	4.89	5.01	0.28	1.11	0.97	7.84	20.1
5D	90	g	4.91	5.30	0.26	1.26	1.04	9.13	21.9
6D	120	g	5.99	7.62	0.32	1.83	1.44	13.30	30.5
7D	1350	g	1.02	7.50	0.17	1.47	0.88	11.17	22.2
8D	3066	g	0.30	13.67	0.34	3.10	1.66	25.14	44.2

Table A4.67 Mass Balance for Water : VP11

Sample No.	Time in Process Stage min	Water in the reactor g	Water off with AD g	Water off with sample g	Total g	Water Produced	
						g	gmol
0	0	1022.83					
M0	22	1022.83					
1M	40	1038.80	-	1.24	1040.04	17.21	0.96
1D	15	1044.23	40.44	4.87	1089.54	50.74	2.82
2D	30	1034.70	43.81	5.05	1083.56	39.33	2.18
3D	45	1015.78	38.10	5.12	1059.00	24.30	1.35
4D	60	989.81	44.60	5.01	1039.42	23.64	1.31
5D	90	870.58	132.37	4.89	1007.84	18.03	1.00
6D	120	726.09	140.04	4.91	871.04	0.46	0.03
7D	1350	153.22	615.58	5.99	774.79	48.70	2.70
8D	3066	21.20	166.44	1.02	188.66	35.44	1.97
9D	4248	15.87	18.22	0.30	34.39	13.19	0.73

Table A4.68 Mass Balance for n-Butanol : VP11

Sample No.	Time in Process Stage min	Butanol in the reactor g	Butanol off with AD g	Butanol off with sample g	Total g	Butanol Reacted	
						g	gmol
0	0	1492.28					
M0	22	1492.28					
1M	40	1439.92	-	1.81	1441.73	50.55	0.68
1D	15	1277.90	0.89	6.76	1285.55	154.37	2.08
2D	30	1168.03	2.80	6.18	1177.01	100.89	1.36
3D	45	1106.84	2.30	5.78	1114.92	53.11	0.72
4D	60	1013.39	2.91	5.45	1021.75	85.09	1.15
5D	90	940.14	8.71	5.01	953.86	59.53	0.80
6D	120	924.35 (+370.05)	8.62	5.30	938.27	1.87	0.03
7D	1350	1124.83	37.50	7.62	1162.95	124.45	1.68
8D	3066	963.88	9.57	7.50	980.95	143.88	1.94
9D	4248	895.77	1.06	13.67	910.50	53.38	0.72

Table A4.69 Mass Balance for Solids : VP11

Sample No.	Time in Process Stage min	Solids in the reactor g	Solids removed with AD g	Solids removed with sample g	Total g	Solids Increase g
0	0	680.00				
M0	22	1227.48	-	-	1227.48	547.48*
1M	40	1357.64	-	1.49	1359.13	98.14* 33.51
1D	15	1455.08	-	6.37	1461.45	103.81
2D	30	1509.57		7.04	1516.61	61.53
3D	45	1531.11	-	7.47	1538.58	29.01
4D	60	1585.33	-	7.55	1592.88	61.77
5D	90	1620.67	-	7.84	1628.51	43.18
6D	120	1612.71	-	9.13	1621.84	1.17
7D	1350	1675.42	-	13.30	1688.72	76.01
8D	3066	1772.84	-	11.17	1784.01	108.59
9D	4248	1787.88	-	25.14	1813.02	40.18

* Solids increase due to methylolation

Table A4.70 Results of the mass balances : VP11

Process Stage	Sample No.	Differential Time Δt min	Water Produced g	Water Produced gmol	n-Butanol Reacted g	n-Butanol Reacted gmol	Solids Increase g
							645.62*
Methylolation	1M		17.21	0.96	50.55	0.68	33.51
Dehydration	1D	15	50.74	2.82	154.37	2.08	103.81
	2D	15	39.33	2.18	100.89	1.36	61.53
	3D	15	24.30	1.35	53.11	0.72	29.01
	4D	15	23.64	1.31	85.09	1.15	61.77
	5D	30	18.03	1.00	59.53	0.80	43.18
	6D	30	0.46	0.03	1.87	0.03	1.17
	7D	1230	48.70	2.70	124.45	1.68	76.01
	8D	1716	35.44	1.97	143.88	1.94	108.59
	9D	1182	13.19	0.73	53.38	0.72	40.18

* Solids increase due to methylolation

Table A4.71 Chemical changes over a differential reaction time : VP11

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X gmol	Methylene ether Produced Y gmol	Methylols Reacted Z gmol
Methylolation	1M		0.68	0.28	1.24
Dehydration	1D	15	2.08	0.74	3.56
	2D	15	1.36	0.82	3.00
	3D	15	0.72	0.63	1.98
	4D	15	1.15	0.16	1.47
	5D	30	0.80	0.20	1.20
	6D	30	0.03	0.00	0.03
	7D	1230	1.68	1.02	3.72
	8D	1716	1.94	0.03	2.00
	9D	1182	0.72	0.01	0.74

Table A4.72 Experimental and Theoretical Solids : VP11

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids g	Theoretical Increase in Solids g
Methylolation	1M		33.51	33.11
Dehydration	1D	15	103.81	103.37
	2D	15	61.53	61.53
	3D	15	29.01	29.05
	4D	15	61.77	61.64
	5D	30	43.18	41.28
	6D	30	1.17	1.68
	7D	1230	76.01	75.88
	8D	1716	108.59	108.30
	9D	1182	40.18	40.22

Table A4.73 Chemical changes as a function of time : VP11

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges gmol	Butyl ether Groups gmol	Methylols gmol
					21.51
Methylolation	1M	40	0.28	0.68	20.27
Dehydration	1D	15	1.02	2.76	16.71
	2D	30	1.84	4.12	13.71
	3D	45	2.47	4.84	11.73
	4D	60	2.63	5.99	10.26
	5D	90	2.83	6.79	9.06
	6D	120	2.83	6.82	9.03
	7D	1350	3.85	8.50	5.31
	8D	3066	3.88	10.44	3.31
	9D	4248	3.89	11.16	2.57

A4.10 EXPERIMENT Works 1

Table A4.74 Raw Materials : Works 1

Material			**Density @ 25 °C**	**Quantity kg**
Melamine	1075	kg		1075.00
Formalin	2738	1	1.1251	3080.52
n-Butanol (1)	3050	1	0.8058	2457.69
				6613.21
Xylol	415	1	0.8609	357.27
n-Butanol (2)	726	1	0.8058	585.01
n-Butanol (3)	100	1	0.8058	80.58
n-Butanol (4)	100	1	0.8058	80.58
n-Butanol (5)	100	1	0.8058	80.58
n-Butanol (6)	150	1	0.8058	120.87
Formalin Compositions			**Wt %**	**Quantity kg**
Formaldehyde			43.89	1352.04
Water			52.61	1620.66
Methanol			3.50	107.82
				3080.52

Initial Molar Ratio

F : M : B = 5.29 : 1 : 3.89 (45.07 : 8.525 : 33.16)

Table A4.75 Initial Charge : Works 1

Material	Quantity kg	Composition % (wt)
Melamine	1075.00	16.26
n-Butanol	2457.69	37.16
Formaldehyde	1352.04	20.44
Water	1620.66	24.51
Methanol	107.82	1.63
Total	6613.21	100.00

Table A4.76 Experimental Detail : Works 1

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off kg	Comments
						Charge Preparation
						2738 l Formalin charged
						3050 l n-Butanol charged
		6.10				1500 ml Caustic added
						1075 kg Melamine charged
						Methylolation
0						Steam on
35	95					Boiling commenced
50	95					Sample 1M 0.22 kg
						Steam off
						Dehydration
						415 l Xylol charged
0						Steam on
40	93				190	Sample 1D 0.20 kg
80	93				345	Sample 2D 0.30 kg
120	94		0.7		562	Sample 3D 0.25 kg
180	96		1.0		908	Sample 4D 0.25 kg
						726 l n-Butanol added
300	104		3.2		1980	Sample 5D 0.24 kg
						Steam off
						Acid Reaction
						3500 ml Acid catalyst added
0						Steam on
60	106		3.5	7.0	2130	Sample 1A 0.23 kg
						100 l n-Butanol added
120	110		4.1	8.0	2245	Sample 2A 0.25 kg
						100 l n-Butanol added
180	118		4.1	15.0	2312	Sample 3A 0.22 kg
						100 l n-Butanol added
240	118		4.0	19.5	2347	Sample 4A 0.22 kg
						150 l n-Butanol added
300	118		3.4	23.0	2371	Sample 5A 0.23 kg
						Steam off, Cooling on.

Table A4.77 Sampling Details : Works 1

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample kg	Wt. of Resin in Reactor including sample kg	Wt. of AD removed kg
Methylolation	1M	50 End of Methylolation	0.22	6613.21	-
Dehydration	1D	40	0.20	6780.26	190
	2D	80	0.30	6625.06	155
	3D	120	0.25	6407.76	217
	4D	180	0.25	6061.51	346
	5D	300	0.24	5574.27	1072
Acid Reaction	1A	60	0.23	5424.03	150
	2A	120	0.25	5389.38	115
	3A	180	0.22	5402.71	67
	4A	240	0.22	5448.07	35
	5A	300	0.23	5544.72	24

Table A4.78 Materials in the Reactor : Works 1

Sample No.	Time in Process Stage min	% or kg	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.51	37.16	1.63	-	20.44	16.26	
		kg	1620.66	2457.69	107.82		1352.04	1075.00	6613.21
1M	50	%	24.81	36.15	1.63	-	5.13	32.28	
		kg	1640.74	2390.68	107.82		339.26	2134.74	6613.21
1D	40	%	24.75	25.33	1.44	5.27	4.86	38.35	
		kg	1678.11	1717.44	97.56	357.27	329.52	2600.23	6780.26
2D	80	%	24.44	22.43	1.36	5.39	4.85	41.53	
		kg	1619.16	1486.00	89.81	357.26	321.32	2751.39	6625.06
3D	120	%	22.52	22.53	1.24	5.58	4.83	43.30	
		kg	1443.03	1443.67	79.39	357.24	309.49	2774.56	6407.76
4D	180	%	18.93	23.40	1.12	5.89	4.79	45.87	
		kg	1147.44	1418.39	67.97	357.23	290.35	2780.41	6061.51
5D	300	%	4.08	34.86	0.83	6.41	3.90	49.92	
		kg	227.43	1943.19	46.53	357.22	217.40	2782.68	5574.27
1A	60	%	3.40	32.06	0.73	6.59	3.87	53.35	
		kg	184.42	1738.94	39.33	357.20	209.91	2893.72	5424.03
2A	120	%	2.25	32.08	0.62	6.63	3.74	54.68	
		kg	121.26	1728.91	33.58	357.18	201.56	2946.91	5389.38
3A	180	%	1.39	32.86	0.55	6.61	3.64	54.95	
		kg	75.10	1775.33	29.96	357.16	196.66	2968.79	5402.71
4A	240	%	0.96	33.61	0.51	6.56	3.56	54.80	
		kg	52.30	1831.10	28.00	357.15	193.95	2985.54	5448.07
5A	300	%	0.61	35.06	0.48	6.44	3.47	53.91	
		kg	33.82	1945.64	26.46	357.14	192.40	2989.16	5544.72

Table A4.79 Materials in AD : Works 1

Sample No.	Time in Process Stage min	% or kg	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	40	%	84.50	5.10	5.40	-	5.00	-	
		kg	160.55	9.69	10.26		9.50		190
2D	80	%	84.60	5.10	5.00	-	5.30	-	
		kg	131.13	7.91	7.75		8.21		155
3D	120	%	85.50	5.20	4.80	-	5.50	-	
		kg	185.53	11.28	10.42		11.93		217
4D	180	%	86.00	5.20	3.30	-	5.50	-	
		kg	297.56	17.99	11.42		19.03		346
5D	300	%	85.90	5.30	2.00	-	6.80	-	
		kg	920.85	56.82	21.44		72.90		1072
1A	60	%	84.50	5.00	4.80	-	5.70	-	
		kg	126.75	7.50	7.20		8.55		150
2A	120	%	82.60	5.10	5.00	-	7.30	-	
		kg	94.99	5.86	5.75		8.39		115
3A	180	%	82.40	5.10	5.40	-	7.10	-	
		kg	55.21	3.42	3.62		4.76		67
4A	240	%	82.40	5.20	5.60	-	6.80	-	
		kg	28.84	1.82	1.96		2.38		35
5A	300	%	82.20	5.40	6.40	-	6.00	-	
		kg	19.73	1.30	1.54		1.44		24

Table A4.80 Materials in Samples : Works 1

Sample No.	Time in Process Stage min	% or kg	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	45	kg	0.05	0.08	-	-	0.01	0.07	0.22
1D	40	kg	0.05	0.05	-	0.01	0.01	0.08	0.20
2D	80	kg	0.07	0.07	-	0.02	0.01	0.12	0.30
3D	120	kg	0.06	0.06	-	0.01	0.01	0.11	0.25
4D	180	kg	0.05	0.06	-	0.01	0.01	0.11	0.25
5D	300	kg	0.01	0.08	-	0.02	0.01	0.12	0.24
1A	60	kg	0.01	0.07	-	0.02	0.01	0.12	0.23
2A	120	kg	0.01	0.08	-	0.02	0.01	0.14	0.25
3A	180	kg	0.00	0.07	-	0.01	0.01	0.12	0.22
4A	240	kg	0.00	0.07	-	0.01	0.01	0.12	0.22

Table A4.81 Mass Balance for Water : Works 1

Sample No.	Time in Process Stage	Water in the reactor	Water off with AD	Water off with sample	Total	Water Produced	
	min	kg	kg	kg	kg	kg	kgmol
0	0	1620.66					
1M	50	1640.74	-	-	1640.74	20.08	1.11
1D	40	1678.11	160.55	0.05	1838.71	197.97	10.99
2D	80	1619.16	131.13	0.05	1750.34	72.23	4.01
3D	120	1443.03	185.53	0.07	1628.63	9.47	0.53
4D	180	1147.44	297.56	0.06	1445.06	2.03	0.11
5D	300	227.43	920.85	0.05	1148.33	0.89	0.05
1A	60	184.42	126.75	0.01	311.18	83.75	4.65
2A	120	121.26	94.99	0.01	216.26	31.84	1.77
3A	180	75.10	55.21	0.01	130.32	9.06	0.50
4A	240	52.30	28.84	0.00	81.14	6.04	0.34
5A	300	33.82	19.73	0.00	53.55	1.25	0.07

Table A4.82 Mass Balance for n-Butanol : Works 1

Sample No.	Time in Process Stage min	Butanol in the reactor kg	Butanol off with AD kg	Butanol off with sample kg	Total kg	Butanol Reacted kg	Butanol Reacted kgmol
0	0	2457.69					
1M	50	2390.68	-	-	2390.68	67.01	0.90
1D	40	1717.44	9.69	0.08	1727.21	663.47	8.95
2D	80	1486.00	7.91	0.05	1493.96	223.48	3.01
3D	120	1443.67	11.28	0.07	1455.02	30.98	0.42
4D	180	1418.39	17.99	0.06	1436.44	7.23	0.10
5D	300	(+585.01) 1943.19	56.82	0.06	2000.07	3.33	0.04
1A	60	1738.94	7.50	0.08	1746.52	196.67	2.65
2A	120	(+80.58) 1728.91	5.86	0.07	1734.84	84.68	1.14
3A	180	(+80.58) 1775.33	3.42	0.08	1778.83	30.66	0.41
4A	240	(+80.58) 1831.10	1.82	0.07	1832.99	22.92	0.31
5A	300	(+120.97) 1945.64	1.30	0.07	1947.01	4.96	0.07

Table A4.83 Mass Balance for Solids : Works 1

Sample No.	Time in Process Stage min	Solids in the reactor kg	Solids removed with AD kg	Solids removed with sample kg	Total kg	Solids Increase kg
0	0	1075.00				
1M	50	2134.74	-	-	2134.74	1012.78* 46.96
1D	40	2600.23	-	0.07	2600.30	465.56
2D	80	2751.39	-	0.08	2751.47	151.24
3D	120	2774.56	-	0.12	2774.68	23.29
4D	180	2780.41	-	0.11	2780.52	5.96
5D	300	2782.68	-	0.11	2782.79	2.38
1A	60	2893.72	-	0.12	2893.84	111.16
2A	120	2946.91	-	0.12	2947.03	53.31
3A	180	2968.79	-	0.14	2968.93	22.02
4A	240	2985.54	-	0.12	2985.66	16.87
5A	300	2989.16	-	0.12	2989.28	3.74

* Solids increase due to methylolation

Table A4.84 Results of the mass balances : Works 1

Process Stage	Sample No.	Differential Time Δt min	Water Produced		n-Butanol Reacted		Solids Increase
			kg	kgmol	kg	kgmol	kg
							1012.78*
Methylolation	1M		20.08	1.11	67.01	0.90	46.96
Dehydration	1D	40	197.97	10.99	663.47	8.95	465.56
	2D	40	72.23	4.01	223.48	3.01	151.24
	3D	40	9.47	0.53	30.98	0.42	23.29
	4D	60	2.03	0.11	7.23	0.10	5.96
	5D	120	0.89	0.05	3.33	0.04	2.38
Acid Reaction	1A	60	83.75	4.65	196.67	2.65	111.16
	2A	60	31.84	1.77	84.68	1.14	53.31
	3A	60	9.06	0.50	30.66	0.41	22.02
	4A	60	6.04	0.34	22.92	0.31	16.87
	5A	60	1.25	0.07	4.96	0.07	3.74

* Solids increase due to methylolation

Table A4.85 Chemical changes over a differential reaction time : Works 1

Process Stage	Sample No.	Differential Time Δt min	Butyl ether Produced X kgmol	Methylene ether Produced Y kgmol	Methylols Reacted Z kgmol
Methylolation	1M		0.90	0.21	1.32
Dehydration	1D	40	8.95	2.04	13.03
	2D	40	3.01	1.00	5.01
	3D	40	0.42	0.11	0.64
	4D	60	0.10	0.01	0.12
	5D	120	0.04	0.01	0.06
Acid Reaction	1A	60	2.65	2.00	6.65
	2A	60	1.14	0.63	2.40
	3A	60	0.41	0.09	0.59
	4A	60	0.31	0.03	0.37
	5A	60	0.07	0.00	0.07

Table A4.86 Experimental and Theoretical Solids : Works 1

Process Stage	Sample No.	Differential Time Δt min	Experimental Increase in Solids kg	Theoretical Increase in Solids kg
Methylolation	1M		46.96	46.71
Dehydration	1D	40	465.56	465.39
	2D	40	151.24	150.86
	3D	40	23.29	21.58
	4D	60	5.96	5.43
	5D	120	2.38	2.06
Acid Reaction	1A	60	111.16	112.65
	2A	60	53.31	52.61
	3A	60	22.02	21.38
	4A	60	16.87	16.85
	5A	60	3.74	3.92

Table A4.87 Chemical changes as a function of time : Works 1

Process Stage	Sample No.	Reaction Time in Process Stage min	Methylene ether Bridges kgmol	Butyl ether Groups kgmol	Methylols kgmol
					33.73
End of Methylolation	1M	40	0.21	0.90	32.41
Dehydration	1D	40	2.25	9.85	19.38
	2D	80	3.25	12.86	14.37
	3D	120	3.36	13.28	13.73
	4D	180	3.37	13.38	13.61
	5D	300	3.38	13.42	13.55
Acid Reaction	1A	60	5.38	16.07	6.90
	2A	120	6.01	17.21	4.50
	3A	180	6.10	17.62	3.91
	4A	240	6.13	17.93	3.54
	5A	300	6.13	18.00	3.47

A4.11 EXPERIMENT Works 2

Table A4.88 Raw Materials : Works 2

Material			**Density @ 25 °C**	**Quantity g**
Melamine	1075	kg		1075.00
Formalin	2738	l	1.1253	3081.07
n-Butanol (1)	3050	l	0.8058	2457.69
				6613.76
Xylol	415	l	0.8609	357.27
n-Butanol (2)	726	l	0.8058	585.01
n-Butanol (3)	200	l	0.8058	161.16
n-Butanol (4)	200	l	0.8058	161.16
Formalin Compositions			**Wt %**	**Quantity g**
Formaldehyde			43.92	1353.20
Water			52.58	1620.03
Methanol			3.50	107.84
				3081.07

Initial Molar Ratio

F : M : B = 5.29 : 1 : 3.89 (45.11 : 8.525 : 33.16)

Table A4.89 Initial Charge : Works 2

Material	Quantity kg	Composition % (wt)
Melamine	1075.00	16.25
n-Butanol	2457.69	37.16
Formaldehyde	1353.20	20.46
Water	1620.03	24.50
Methanol	107.84	1.63
Total	6613.76	100.00

Table A4.90 Experimental Detail : Works 2

Time in Process Stage min	Reactor Temp. °C	pH	Viscosity @ 25 °C Poise	Solvent Tolerance @ 20 °C ml	AD off kg	Comments
						Charge Preparation
						2738 l Formalin charged
		4.80				3050 l n-Butanol charged
		6.00				550 ml Caustic added
						1075 kg Melamine charged
						Methylolation
0						Steam on
30	95					Boiling commenced
45	95					Sample 1M 0.20 kg
						Steam off
						Dehydration
						415 l Xylol charged
0						Steam on
40	95				517	Sample 1D 0.21 kg
80	95				852	Sample 2D 0.21 kg
120	95		0.70		1234	Sample 3D 0.23 kg
170	97		1.60		1664	Sample 4D 0.26 kg
						726 l n-Butanol added
265	104				2066	Sample 5D 0.25 kg
						Steam off
						Acid Reaction
						4500 ml Acid catalyst added
0						Steam on
60	104		2.80	5.9	2258	Sample 1A 0.25 kg
120	108		3.75	11.2	2400	Sample 2A 0.24 kg
						200 l n-Butanol added
180	114		3.45	17.7	2473	Sample 3A 0.23 kg
						200 l n-Butanol added
240	117		2.90	22.8	2517	Sample 4A 0.24 kg
300	119		3.20	26.8	2547	Sample 5A 0.25 kg
						Steam off, Cooling on.

Table A4.91 Sampling Details : Works 2

Process Stage	Sample No.	Time in each Process Stage min	Wt. of Resin Sample kg	Wt. of Resin in Reactor including sample kg	Wt. of AD removed kg
Methylolation	1M	45 End of Methylolation	0.20	6613.76	-
Dehydration	1D	40	0.21	6453.83	517
	2D	80	0.21	6118.62	335
	3D	120	0.23	5736.41	382
	4D	170	0.26	5306.18	430
	5D	265	0.25	5488.93	402
Acid Reaction	1A	60	0.25	5296.68	192
	2A	120	0.24	5154.43	142
	3A	180	0.23	5242.35	73
	4A	240	0.24	5359.28	44
	5A	300	0.25	5329.04	30

Table A4.92 Materials in the Reactor : Works 2

Sample No.	Time in Process Stage min	% or kg	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
0	0	%	24.50	37.16	1.63	-	20.46	16.25	
		kg	1620.03	2457.69	107.84		1353.20	1075.00	6613.76
1M	45	%	24.94	35.88	1.63	-	5.00	32.55	
		kg	1649.48	2373.02	107.84		330.69	2152.96	6613.76
1D	40	%	23.30	24.24	1.24	5.54	4.72	40.96	
		kg	1503.74	1564.41	79.92	357.27	304.62	2643.49	6453.83
2D	80	%	20.45	24.12	1.04	5.84	4.68	43.87	
		kg	1251.26	1475.81	63.84	357.26	286.35	2684.24	6118.62
3D	120	%	16.27	24.94	0.89	6.23	4.62	47.05	
		kg	933.31	1430.66	51.23	357.25	265.11	2698.98	5736.41
4D	170	%	10.60	26.44	0.76	6.73	4.54	50.93	
		kg	562.46	1402.95	40.48	357.24	240.90	2702.44	5306.18
5D	265	%	3.90	35.77	0.61	6.51	3.95	49.26	
		kg	214.07	1963.39	33.65	357.22	216.81	2703.85	5488.93
1A	60	%	3.35	31.70	0.47	6.74	3.88	53.86	
		kg	177.44	1679.05	25.01	357.20	205.51	2852.79	5296.68
2A	120	%	2.10	29.95	0.35	6.93	3.77	56.90	
		kg	108.24	1543.75	18.19	357.18	194.32	2932.87	5154.43
3A	180	%	1.40	31.01	0.28	6.81	3.60	56.90	
		kg	73.39	1625.65	14.54	357.16	188.72	2982.90	5242.35
4A	240	%	0.81	32.94	0.23	6.66	3.46	55.90	
		kg	43.41	1765.35	12.16	357.14	185.43	2995.84	5359.28
5A	300	%	0.38	33.03	0.19	6.70	3.44	56.26	
		kg	20.25	1760.18	10.27	357.12	183.32	2998.12	5329.04

Table A4.93 Materials in AD : Works 2

Sample No.	Time in Process Stage min	% or kg	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1D	40	%	84.50	5.10	5.40	-	5.00	-	
		kg	436.87	26.37	27.92		25.85		517
2D	80	%	84.60	5.20	4.80	-	5.40	-	
		kg	283.41	17.42	16.08		18.09		335
3D	120	%	85.90	5.20	3.30	-	5.60	-	
		kg	328.14	19.86	12.61		21.39		382
4D	170	%	86.70	5.20	2.50	-	5.60	-	
		kg	372.81	22.36	10.75		24.08		430
5D	265	%	86.90	5.40	1.70	-	6.00	-	
		kg	349.34	21.71	6.83		24.12		402
1A	60	%	84.50	5.00	4.50	-	6.00	-	
		kg	162.24	9.60	8.64		11.52		192
2A	120	%	82.50	5.00	4.80	-	7.70	-	
		kg	117.15	7.10	6.82		10.93		142
3A	180	%	82.70	5.00	5.00	-	7.30	-	
		kg	60.37	3.65	3.65		5.33		73
4A	240	%	82.50	5.20	5.40	-	6.90	-	
		kg	36.30	2.29	2.38		3.04		44
5A	300	%	82.40	5.40	6.30	-	6.00	-	
		kg	24.72	1.62	1.89		1.80		30

Table A4.94 Materials in Samples : Works 2

Sample No.	Time in Process Stage min	% or kg	Water	n-Butanol	Methanol	Xylol	F.F.	Solids (Vac.)	Total
1M	45	kg	0.05	0.07	-	-	0.01	0.07	0.20
1D	40	kg	0.05	0.05	-	0.01	0.01	0.09	0.21
2D	80	kg	0.04	0.05	-	0.01	0.01	0.09	0.21
3D	120	kg	0.04	0.06	-	0.01	0.01	0.11	0.23
4D	170	kg	0.03	0.07	-	0.02	0.01	0.13	0.26
5D	265	kg	0.01	0.09	-	0.02	0.01	0.12	0.25
1A	60	kg	0.01	0.08	-	0.02	0.01	0.13	0.25
2A	120	kg	0.00	0.07	-	0.02	0.01	0.14	0.24
3A	180	kg	0.00	0.07	-	0.02	0.01	0.13	0.23
4A	240	kg	0.00	0.08	-	0.02	0.01	0.13	0.24

Table A4.95 Mass Balance for n-Butanol : Works 2

Sample No.	Time in Process Stage min	Butanol in the reactor kg	Butanol off with AD kg	Butanol off with sample kg	Total kg	Butanol Reacted kg	kgmol
0	0	2457.69					
1M	45	2373.02	-	-	2373.02	84.67	1.14
1D	40	1564.41	26.37	0.07	1590.85	782.17	10.55
2D	80	1475.81	17.42	0.05	1493.28	71.13	0.96
3D	120	1430.66	19.86	0.05	1450.57	25.24	0.34
4D	170	1402.95	22.36	0.06	1425.37	5.29	0.07
5D	265	(+585.01) 1963.39	21.71	0.07	1985.17	2.79	0.04
1A	60	1679.05	9.60	0.09	1688.74	274.65	3.71
2A	120	1543.75	7.10	0.08	1550.93	128.12	1.73
3A	180	(+161.16) 1625.65	3.65	0.07	1629.37	75.54	1.02
4A	240	(+161.16) 1765.35	2.29	0.07	1767.71	19.10	0.26
5A	300	1760.18	1.62	0.08	1761.88	3.47	0.05

Table A4.96 Mass Balance for Solids : Works 2

Sample No.	Time in Process Stage min	Solids in the reactor kg	Solids removed with AD kg	Solids removed with sample kg	Total kg	Solids Increase kg
0	0	1075.00				
1M	45	2152.96	-	-	2152.96	1022.51* 55.45
1D	40	2643.49	-	0.07	2643.56	490.60
2D	80	2684.24	-	0.09	2684.33	40.84
3D	120	2698.98	-	0.09	2699.07	14.83
4D	170	2702.44	-	0.11	2702.55	3.57
5D	265	2703.85	-	0.13	2703.98	1.54
1A	60	2852.79	-	0.12	2852.91	149.06
2A	120	2932.87	-	0.13	2933.00	80.21
3A	180	2982.90	-	0.14	2983.04	50.17
4A	240	2995.84	-	0.13	2995.97	13.07
5A	300	2998.12	-	0.13	2998.25	2.41

* Solids increase due to methylolation

APPENDIX 5

COMPUTER PROGRAMS AND SIMULATION DATA

A5.1 Program for fitting Tomita's Experimental Data

```
   INTEGER P,R,F1,F2,J,K
   REAL K1,K2,T,E,CN1,CN2,CM1,CM2,DT,N1,N2,M1,M2,M3,M4,M5,M6,M7,M8
   REAL X(15),D(15)
   REAL NL,NG,M9,M10,P1,P2,P3,P4,P5,P6,P7,P8,P9,P10

   COMMON /ONE/J,K
   COMMON /TWO/DT
   COMMON /THREE/XA,DXA
   COMMON /FOUR/TD

   DATA H,E,R,P /0.1,330,4,10/

   PRINT*,"INPUT VALUE OF NG"
   READ*,NG
   PRINT*,"INPUT VALUE OF NL"
   READ*,NL

   N1=NL**(0.5)
   N2=1/N1

   M1=NG**2
   M2=1/M1
   M3=NG**3
   M4=1/M3
   M5=NG**4
   M6=1/M5
   M7=NG**5
   M8=1/M7
   M9=2/NG
   M10=4*NG

   P1=NG*N1
   P2=2*N2*(1/NG)
   P3=2*M1*N1
   P4=2*M2*N2
   P5=M3*N1
   P6=2*M4*N2
   P7=2*M5*N1
   P8=4*M6*N2
   P9=M7*N1
   P10=6*M8*N2

   PRINT*,"INPUT VALUE OF K1"
   READ*,K1
   K2=K1*0.2208233

   DO 10 I=1,15
     X(I)=0
10 CONTINUE
```

```
 X(1)=0.0325
 X(11)=0.167
 PRINT
 PRINT
PRINT*,"==========================================================
*=============="
 PRINT*,"  TIME          MELAMINE      METHYLOL1     METHYLOL2
* METHYLOL3   "
 PRINT*,"  TIME          METHYLOL4     METHYLOL5     METHYLOL6
* METHYLOL7   "
 PRINT*,"  TIME          METHYLOL8     METHYLOL9     FORMALDE.  "
 PRINT*,"  MIN.          MOL/L         MOL/L         MOL/L
* MOL/L      "
PRINT*,"==========================================================
*=============="
 PRINT
 PRINT

 CALL ZERO(T)
 DO

 D(1)=K2*X(2)-6*K1*X(1)*X(11)
 D(2)=6*K1*X(1)*X(11)+K2*X(3)*M9+K2*X(5)*P2-K2*X(2)-K1*X(2)*X(11)
**M10-K1*X(2)*X(11)*P1
 D(3)=K1*X(2)*X(11)*M10+K2*X(4)*3*M2+K2*X(6)*P4-K2*X(3)*M9
*-K1*X(3)*X(11)*2*M1-K1*X(3)*X(11)*P3
 D(4)=K1*X(3)*X(11)*2*M1+K2*X(7)*P6-K2*X(4)*3*M2-K1*X(4)*X(11)*3*P5
 D(5)=K1*X(2)*X(11)*P1+K2*X(6)*M2-K2*X(5)*P2-K1*X(5)*X(11)*4*M1
 D(6)=K1*X(3)*X(11)*P3+K1*X(5)*X(11)*4*M1+K2*X(7)*2*M4+K2*X(8)*
*2*P6-K2*X(6)*P4-K2*X(6)*M2-K1*X(6)*X(11)*2*M3-K1*X(6)*X(11)*P5
 D(7)=K1*X(4)*X(11)*3*P5+K1*X(6)*X(11)*2*M3+K2*X(9)*P8-K2*X(7)*
*P6-K2*X(7)*2*M4-K1*X(7)*X(11)*P7
 D(8)=K1*X(6)*X(11)*P5+K2*X(9)*M6-K2*X(8)*2*P6-K1*X(8)*X(11)*2*M5
 D(9)=K1*X(7)*X(11)*P7+K1*X(8)*X(11)*2*M5+K2*X(10)*P10-K2*X(9)*
*P8-K2*X(9)*M6-K1*X(9)*X(11)*P9
 D(10)=K1*X(9)*X(11)*P9-K2*X(10)*P10
 CN1=X(2)+X(3)*M9+X(5)*P2+X(4)*3*M2+X(6)*P4+X(7)*P6+X(6)*M2
 CN2=X(7)*2*M4+X(8)*2*P6+X(9)*P8+X(9)*M6+X(10)*P10
 CM1=X(1)*6+X(2)*M10+X(2)*P1+X(3)*2*M1+X(3)*P3+X(4)*3*P5+
*X(5)*4*M1
 CM2=X(6)*2*M3+X(6)*P5+X(7)*P7+X(8)*2*M5+X(9)*P9
 D(11)=K2*(CN1+CN2)-K1*X(11)*(CM1+CM2)

 CALL PRNTF (P,E-H/2,F1,F2,T)

 IF (F2.EQ.2) THEN
   PRINT*,T,X(1),X(2),X(3),X(4)
   PRINT*,T,X(5),X(6),X(7),X(8)
   PRINT*,T,X(9),X(10),X(11)
   PRINT
 ENDIF

 CALL INTI (T,H,R)
 CALL INTX (X,D,R)

 UNTIL (F1.EQ.2)

 END
```

A5.2 Model Solution for Fitting Tomita's Experimental Data

```
>SIMRUN

INPUT VALUE OF NG
>0.93

INPUT VALUE OF NL
>0.59

INPUT VALUE OF K1
>0.016


==========================================================================
 TIME       MELAMINE       METHYLOL1      METHYLOL2      METHYLOL3
 TIME       METHYLOL4      METHYLOL5      METHYLOL6      METHYLOL7
 TIME       METHYLOL8      METHYLOL9      FORMALDE.
 MIN.       MOL/L          MOL/L          MOL/L          MOL/L
==========================================================================


 0.0000     3.25000E-02    0.0000         0.0000         0.0000
 0.0000     0.0000         0.0000         0.0000         0.0000
 0.0000     0.0000         0.0000         0.16700

 10.0000    2.78308E-02    4.40579E-03    2.15469E-04    3.25537E-06
 10.0000    4.09161E-05    3.70817E-06    7.78588E-08    1.47775E-08
 10.0000    5.74859E-10    1.31002E-12    0.16206

 20.000     2.40723E-02    7.52149E-03    7.23547E-04    2.14286E-05
 20.000     1.35882E-04    2.41350E-05    9.89681E-07    1.85686E-07
 20.000     1.40533E-08    6.13319E-11    0.15762

 30.000     2.10185E-02    9.71585E-03    1.37807E-03    5.99726E-05
 30.000     2.55985E-04    6.67996E-05    4.01055E-06    7.43984E-07
 30.000     8.21348E-08    5.14877E-10    0.15362

 40.000     1.85155E-02    1.12486E-02    2.08992E-03    1.18744E-04
 40.000     3.84059E-04    1.30823E-04    1.02183E-05    1.87462E-06
 40.000     2.68271E-07    2.14743E-09    0.15000

 50.000     1.64472E-02    1.23044E-02    2.80594E-03    1.95044E-04
 50.000     5.10223E-04    2.12598E-04    2.02461E-05    3.67418E-06
 50.000     6.38835E-07    6.12297E-09    0.14674

 60.000     1.47253E-02    1.30154E-02    3.49552E-03    2.85251E-04
 60.000     6.29088E-04    3.07694E-04    3.42864E-05    6.15676E-06
 60.000     1.24836E-06    1.37572E-08    0.14379

 70.000     1.32818E-02    1.34769E-02    4.14225E-03    3.85661E-04
 70.000     7.38015E-04    4.11798E-04    5.21859E-05    9.27528E-06
 70.000     2.13194E-06    2.62722E-08    0.14111
```

80.000	1.20636E-02	1.37580E-02	4.73848E-03	4.92885E-04
80.000	8.36025E-04	5.21127E-04	7.35559E-05	1.29442E-05
80.000	3.30358E-06	4.46119E-08	0.13869	
90.000	1.10294E-02	1.39092E-02	5.28191E-03	6.04018E-04
90.000	9.23108E-04	6.32563E-04	9.78708E-05	1.70585E-05
90.000	4.75818E-06	6.93435E-08	0.13649	
100.000	1.01465E-02	1.39674E-02	5.77341E-03	7.16665E-04
100.000	9.99796E-04	7.43651E-04	1.24544E-04	2.15077E-05
100.000	6.47551E-06	1.00636E-07	0.13449	
110.00	9.38868E-03	1.39596E-02	6.21567E-03	8.28918E-04
110.00	1.06690E-03	8.52532E-04	1.52983E-04	2.61848E-05
110.00	8.42457E-06	1.38295E-07	0.13267	
120.00	8.73511E-03	1.39058E-02	6.61224E-03	9.39301E-04
120.00	1.12534E-03	9.57854E-04	1.82625E-04	3.09926E-05
120.00	1.05678E-05	1.81828E-07	0.13102	
130.00	8.16888E-03	1.38207E-02	6.96710E-03	1.04670E-03
130.00	1.17608E-03	1.05868E-03	2.12959E-04	3.58460E-05
130.00	1.28646E-05	2.30525E-07	0.12952	
140.00	7.67624E-03	1.37150E-02	7.28424E-03	1.15032E-03
140.00	1.22000E-03	1.15440E-03	2.43534E-04	4.06734E-05
140.00	1.52742E-05	2.83537E-07	0.12815	
150.00	7.24596E-03	1.35968E-02	7.56752E-03	1.24958E-03
150.00	1.25797E-03	1.24467E-03	2.73970E-04	4.54163E-05
150.00	1.77575E-05	3.39951E-07	0.12690	
160.00	6.86876E-03	1.34718E-02	7.82055E-03	1.34414E-03
160.00	1.29075E-03	1.32932E-03	3.03948E-04	5.00287E-05
160.00	2.02788E-05	3.98843E-07	0.12577	
170.00	6.53700E-03	1.33443E-02	8.04663E-03	1.43378E-03
170.00	1.31902E-03	1.40836E-03	3.33211E-04	5.44756E-05
170.00	2.28062E-05	4.59323E-07	0.12473	
180.00	6.24428E-03	1.32171E-02	8.24877E-03	1.51841E-03
180.00	1.34339E-03	1.48188E-03	3.61561E-04	5.87316E-05
180.00	2.53120E-05	5.20569E-07	0.12379	
190.00	5.98526E-03	1.30926E-02	8.42964E-03	1.59805E-03
190.00	1.36438E-03	1.55006E-03	3.88844E-04	6.27795E-05
190.00	2.77731E-05	5.81846E-07	0.12293	
200.00	5.75545E-03	1.29722E-02	8.59164E-03	1.67278E-03
200.00	1.38246E-03	1.61311E-03	4.14953E-04	6.66089E-05
200.00	3.01706E-05	6.42515E-07	0.12214	
210.00	5.55104E-03	1.28568E-02	8.73690E-03	1.74271E-03
210.00	1.39804E-03	1.67131E-03	4.39814E-04	7.02148E-05
210.00	3.24897E-05	7.02035E-07	0.12142	

220.00	5.36882E-03	1.27470E-02	8.86729E-03	1.80802E-03
220.00	1.41146E-03	1.72492E-03	4.63386E-04	7.35967E-05
220.00	3.47188E-05	7.59965E-07	0.12077	
230.00	5.20602E-03	1.26433E-02	8.98447E-03	1.86889E-03
230.00	1.42301E-03	1.77423E-03	4.85649E-04	7.67574E-05
230.00	3.68499E-05	8.15954E-07	0.12017	
240.00	5.06031E-03	1.25457E-02	9.08991E-03	1.92555E-03
240.00	1.43296E-03	1.81953E-03	5.06608E-04	7.97026E-05
240.00	3.88774E-05	8.69736E-07	0.11963	
250.00	4.92964E-03	1.24542E-02	9.18488E-03	1.97819E-03
250.00	1.44154E-03	1.86110E-03	5.26280E-04	8.24396E-05
250.00	4.07982E-05	9.21117E-07	0.11913	
260.00	4.81226E-03	1.23688E-02	9.27053E-03	2.02704E-03
260.00	1.44892E-03	1.89921E-03	5.44696E-04	8.49774E-05
260.00	4.26111E-05	9.69971E-07	0.11868	
270.00	4.70667E-03	1.22892E-02	9.34785E-03	2.07233E-03
270.00	1.45528E-03	1.93413E-03	5.61896E-04	8.73256E-05
270.00	4.43164E-05	1.01622E-06	0.11826	
280.00	4.61155E-03	1.22152E-02	9.41774E-03	2.11427E-03
280.00	1.46076E-03	1.96609E-03	5.77928E-04	8.94945E-05
280.00	4.59158E-05	1.05985E-06	0.11788	
290.00	4.52574E-03	1.21466E-02	9.48096E-03	2.15308E-03
290.00	1.46548E-03	1.99533E-03	5.92843E-04	9.14948E-05
290.00	4.74119E-05	1.10087E-06	0.11753	
300.00	4.44825E-03	1.20830E-02	9.53822E-03	2.18895E-03
300.00	1.46954E-03	2.02207E-03	6.06697E-04	9.33370E-05
300.00	4.88081E-05	1.13931E-06	0.11722	
310.00	4.37818E-03	1.20242E-02	9.59012E-03	2.22209E-03
310.00	1.47304E-03	2.04652E-03	6.19546E-04	9.50316E-05
310.00	5.01083E-05	1.17524E-06	0.11693	
320.00	4.31477E-03	1.19699E-02	9.63721E-03	2.25269E-03
320.00	1.47605E-03	2.06886E-03	6.31448E-04	9.65887E-05
320.00	5.13168E-05	1.20876E-06	0.11666	
330.00	4.25732E-03	1.19197E-02	9.67996E-03	2.28092E-03
330.00	1.47864E-03	2.08927E-03	6.42458E-04	9.80181E-05
330.00	5.24384E-05	1.23995E-06	0.11642	

A5.3 Program for the Simulation of the Methylolation Stage

```
  INTEGER P,R,F1,F2,J,K,N
  REAL K1,K2,T,E,CN1,CN2,CM1,CM2,DT,N1,N2,M1,M2,M3,M4,M5,M6,M7,M8
  REAL X(15),D(15),A(21),B(21),C1(5),C2(5)
  REAL NL,NG,M9,M10,P1,P2,P3,P4,P5,P6,P7,P8,P9,P10
  REAL TMP0,LNK01,LNK02,LNK1,LNK2,T0INV,SLP1,SLP2,TMP,TMP1,TMP2,TINV

  COMMON /ONE/J,K
  COMMON /TWO/DT
  COMMON /THREE/XA,DXA
  COMMON /FOUR/TD

  DATA H,E,R,P /0.1,40,4,2/
  DATA C1(1),C1(2),C1(3),C1(4),C1(5) /0,10,20,30,40/
  DATA C2(1),C2(2),C2(3),C2(4),C2(5) /6.73,6.25,2.96,1.72,1.70/

  NG=0.93
  NL=0.59

  N1=NL**(0.5)
  N2=1/N1

  M1=NG**2
  M2=1/M1
  M3=NG**3
  M4=1/M3
  M5=NG**4
  M6=1/M5
  M7=NG**5
  M8=1/M7
  M9=2/NG
  M10=4*NG

  P1=NG*N1
  P2=2*N2*(1/NG)
  P3=2*M1*N1
  P4=2*M2*N2
  P5=M3*N1
  P6=2*M4*N2
  P7=2*M5*N1
  P8=4*M6*N2
  P9=M7*N1
  P10=6*M8*N2

  N=1

  DO 10 I=1,15
    X(I)=0
10 CONTINUE
  X(1)=1.275
  X(11)=6.731

  TMP0=28
  TMP1=32
  TMP2=43
```

```
*  SET INITIAL LNK1 AND LNK2

   LNK01=-12.35
   LNK02=-14.00

   T0INV=3.333

*  SET SLOPES OF THE ARRHENIUS PLOTS

   SLP1=-11.85
   SLP2=-12.60

   PRINT
   PRINT
  PRINT*,"========================================================
  *==============="
   PRINT*,"  TIME        MELAMINE     METHYLOL1    METHYLOL2
  * METHYLOL3   "
   PRINT*,"  TIME        METHYLOL4    METHYLOL5    METHYLOL6
  * METHYLOL7   "
   PRINT*,"  TIME        METHYLOL8    METHYLOL9    FORMALDE.  "
   PRINT*,"  MIN.        MOL/L        MOL/L        MOL/L
  * MOL/L      "
  PRINT*,"========================================================
  *==============="
   PRINT
   PRINT

   CALL ZERO(T)

   DO

*  TEMPERATURE AS A FUNCTION OF TIME

   IF (T.LE.5) THEN
     TMP=TMP0+0.8*T
   ELSEIF (T.GT.5 .AND. T.LE.10) THEN
     TMP=TMP1+2.2*(T-5)
   ELSEIF (T.GT.10 .AND. T.LE.25) THEN
     TMP=TMP2+3.333*(T-10)
   ELSEIF (T.GT.25) THEN
     TMP=94
   ENDIF

*  EFFECT OF TEMPERATURE ON THE RATE CONSTANTS

   TINV=1000/(TMP+273)
   LNK1=LNK01+SLP1*(TINV-T0INV)
   LNK2=LNK02+SLP2*(TINV-T0INV)
   K1=EXP(LNK1)
   K2=EXP(LNK2)
   K1=K1*60
   K2=K2*60
```

```
*  METHYLOLATION MODEL

    D(1)=K2*X(2)-6*K1*X(1)*X(11)
    D(2)=6*K1*X(1)*X(11)+K2*X(3)*M9+K2*X(5)*P2-K2*X(2)-K1*X(2)*X(11)
   **M10-K1*X(2)*X(11)*P1
    D(3)=K1*X(2)*X(11)*M10+K2*X(4)*3*M2+K2*X(6)*P4-K2*X(3)*M9
   *-K1*X(3)*X(11)*2*M1-K1*X(3)*X(11)*P3
    D(4)=K1*X(3)*X(11)*2*M1+K2*X(7)*P6-K2*X(4)*3*M2-K1*X(4)*X(11)*3*P5
    D(5)=K1*X(2)*X(11)*P1+K2*X(6)*M2-K2*X(5)*P2-K1*X(5)*X(11)*4*M1
    D(6)=K1*X(3)*X(11)*P3+K1*X(5)*X(11)*4*M1+K2*X(7)*2*M4+K2*X(8)*
   *2*P6-K2*X(6)*P4-K2*X(6)*M2-K1*X(6)*X(11)*2*M3-K1*X(6)*X(11)*P5
    D(7)=K1*X(4)*X(11)*3*P5+K1*X(6)*X(11)*2*M3+K2*X(9)*P8-K2*X(7)*
   *P6-K2*X(7)*2*M4-K1*X(7)*X(11)*P7
    D(8)=K1*X(6)*X(11)*P5+K2*X(9)*M6-K2*X(8)*2*P6-K1*X(8)*X(11)*2*M5
    D(9)=K1*X(7)*X(11)*P7+K1*X(8)*X(11)*2*M5+K2*X(10)*P10-K2*X(9)*
   *P8-K2*X(9)*M6-K1*X(9)*X(11)*P9
    D(10)=K1*X(9)*X(11)*P9-K2*X(10)*P10
    CN1=X(2)+X(3)*M9+X(5)*P2+X(4)*3*M2+X(6)*P4+X(7)*P6+X(6)*M2
    CN2=X(7)*2*M4+X(8)*2*P6+X(9)*P8+X(9)*M6+X(10)*P10
    CM1=X(1)*6+X(2)*M10+X(2)*P1+X(3)*2*M1+X(3)*P3+X(4)*3*P5+
   *X(5)*4*M1
    CM2=X(6)*2*M3+X(6)*P5+X(7)*P7+X(8)*2*M5+X(9)*P9
    D(11)=K2*(CN1+CN2)-K1*X(11)*(CM1+CM2)

    CALL PRNTF (P,E-H/2,F1,F2,T)

    IF (F2.EQ.2) THEN
      PRINT*,T,X(1),X(2),X(3),X(4)
      PRINT*,T,X(5),X(6),X(7),X(8)
      PRINT*,T,X(9),X(10),X(11)
      PRINT
      A(N)=T
      B(N)=X(11)
      N=N+1
    ENDIF

    CALL INTI (T,H,R)

    CALL INTX (X,D,R)

    UNTIL (F1.EQ.2)

    CALL GRFFRM (A,B,C1,C2)

    END
```

```
      SUBROUTINE GRFFRM (A,B,C1,C2)

*     TO DRAW A FORMALDEHYDE / TIME PLOT

      REAL A(21),B(21),C1(5),C2(5)

      CALL T4010
      CALL SHIFT2 (30.0,20.0)
      CALL AXIPOS (0,0.0,0.0,120.0,1)
      CALL AXIPOS (0,0.0,0.0,110.0,2)
      CALL AXISCA (2,8,0.0,40.0,1)
      CALL AXISCA (2,7,0.0,7.0,2)
      CALL AXIDRA (1,1,1)
      CALL AXIDRA (-1,-1,2)
      CALL MOVTO2 (30.0,-15.0)
      CALL CHAHOL (18HT*LIME *UM*LIN.*.)
      CALL MOVTO2 (-15.0,30.0)
      CALL CHAANG (90.0)
      CALL CHAHOL (28HF*LORMALDEHYDE *UM*LOL/L.*.)
      CALL CHAANG (0.0)
      CALL GRACUR (A,B,21)
      CALL GRASYM (C1,C2,5,1,0)
      CALL DEVEND
      RETURN
      END
```

A5.4 'SIMLIB' Library Subroutines

```
      SUBROUTINE ZERO (T)

*     TO INITIALISE VARIABLES AND TO SET T TO ZERO

      INTEGER J,K
      REAL T,TD,DXA(15),XA(15)
      COMMON /ONE/J,K
      COMMON /THREE/XA,DXA
      COMMON /FOUR/TD

      T=0
      J=0
      K=0
      TD=0
      DO 40 I=1,15
        DXA(I)=0
        XA(I)=0
   40 CONTINUE
      RETURN
      END


      SUBROUTINE PRNTF (P,E,F1,F2,T)

*     P IS INTERVAL BETWEEN PRINTING IN UNITS OF T
*     E IS FINAL VALUE OF T FOR INTEGRATION

      INTEGER F1,F2,P
      REAL T,TP,DT
      COMMON /TWO/DT

      IF (T.EQ.0) THEN
        F1=1
        TP=0
      ENDIF

      IF (T.NE.0) THEN
        IF (T.LT.TP-DT/2) THEN
          F2=1
          RETURN
        ENDIF
      ENDIF

      F2=2
      TP=TP+P

      IF (T.GE.E) THEN
        F1=2
        TP=0
      ENDIF

      RETURN
      END
```

```
      SUBROUTINE INTI (T,H,R)

*     TO UPDATE T USING STEPLENGTH H AND EITHER MODIFIED
*     EULER (R=2) OR RUNGE KUTTA (R=4) INTEGRATION METHODS

      INTEGER J,K,R
      REAL H,T,TD,DT
      COMMON /ONE/J,K
      COMMON /TWO/DT
      COMMON /FOUR/TD

      IF (R.EQ.2) THEN
        J=J+1
        IF (J.EQ.3) THEN
          J=1
        ELSEIF (J.EQ.2) THEN
          RETURN
        ENDIF
        DT=H
        TD=TD+DT
        T=TD
        RETURN
      ENDIF

      IF (R.EQ.4) THEN
        K=K+1
        IF (K.EQ.5) THEN
          K=1
        ENDIF
        IF (K.EQ.1) THEN
          DT=H/2
          TD=TD+DT
          T=TD
          RETURN
        ELSEIF (K.EQ.3) THEN
          TD=TD+DT
          DT=2*DT
          T=TD
        ENDIF
      RETURN
      ENDIF

      END
```

```
      SUBROUTINE INTX (X,D,R)

*     TO UPDATE X (DEPENDENT VARIABLE) USING D (DERIVATIVE)

      INTEGER J,K,R
      REAL X(15),D(15),XA(15),DXA(15)
      COMMON /ONE/J,K
      COMMON /TWO/DT
      COMMON /THREE/XA,DXA

      IF (R.EQ.2) THEN
        DO 50 I=1,15
          IF (J.EQ.1) THEN
            DXA(I)=D(I)
            X(I)=X(I)+D(I)*DT
          ELSEIF (J.EQ.2) THEN
            X(I)=X(I)+(D(I)-DXA(I))*DT/2
          ENDIF
 50     CONTINUE
        RETURN
      ENDIF

      IF (R.EQ.4) THEN
        DO 60 I=1,15
          IF (K.EQ.1) THEN
            XA(I)=X(I)
            DXA(I)=D(I)
            X(I)=X(I)+D(I)*DT
          ELSEIF (K.EQ.2) THEN
            DXA(I)=DXA(I)+2*D(I)
            X(I)=XA(I)+D(I)*DT
          ELSEIF (K.EQ.3) THEN
            DXA(I)=DXA(I)+2*D(I)
            X(I)=XA(I)+D(I)*DT
          ELSEIF (K.EQ.4) THEN
            DXA(I)=(DXA(I)+D(I))/6
            X(I)=XA(I)+DXA(I)*DT
          ENDIF
 60     CONTINUE
        RETURN
      ENDIF

      END
```

A5.5 Simulation of the Methylolation Stage

```
==========================================================================
 TIME      MELAMINE      METHYLOL1     METHYLOL2     METHYLOL3
 TIME      METHYLOL4     METHYLOL5     METHYLOL6     METHYLOL7
 TIME      METHYLOL8     METHYLOL9     FORMALDE.
 MIN.      MOL/L         MOL/L         MOL/L         MOL/L
==========================================================================


 0.0000    1.2750        0.0000        0.0000        0.0000
 0.0000    0.0000        0.0000        0.0000        0.0000
 0.0000    0.0000        0.0000        6.7310

 2.0000    1.2417        3.29331E-02   2.70689E-04   6.89589E-07
 2.0000    5.19480E-05   7.94058E-07   2.82170E-09   5.41543E-10
 2.0000    3.57920E-12   1.40741E-15   6.6974

 4.0000    1.2022        7.11825E-02   1.30569E-03   7.42019E-06
 4.0000    2.50384E-04   8.53813E-06   6.76569E-08   1.29758E-08
 4.0000    1.91168E-10   1.67392E-13   6.6567

 6.0000    1.1535        0.11702       3.67614E-03   3.57639E-05
 6.0000    7.04264E-04   4.11140E-05   5.57522E-07   1.06832E-07
 6.0000    2.69251E-09   4.02854E-12   6.6050

 8.0000    1.0773        0.18561       9.89525E-03   1.63262E-04
 8.0000    1.89262E-03   1.87394E-04   4.30709E-06   8.24100E-07
 8.0000    3.51850E-08   8.90100E-11   6.5207

10.0000    0.96031       0.28252       2.56848E-02   7.21800E-04
10.0000    4.89899E-03   8.26304E-04   3.23166E-05   6.16779E-06
10.0000    4.47679E-07   1.91908E-09   6.3825

 12.000    0.77315       0.41315       6.80584E-02   3.45756E-03
 12.000    1.29118E-02   3.93805E-03   2.77910E-04   5.27837E-05
 12.000    6.90108E-06   5.29547E-08   6.1324

 14.000    0.50084       0.53008       0.17205       1.71404E-02
 14.000    3.22776E-02   1.93159E-02   2.66272E-03   5.00645E-04
 14.000    1.27398E-04   1.87805E-06   5.6696

 16.000    0.22536       0.49419       0.32893       6.65662E-02
 16.000    6.03511E-02   7.34539E-02   2.04143E-02   3.76241E-03
 16.000    1.91667E-03   5.51353E-05   4.9316

 18.000    6.07158E-02   0.28306       0.39295       0.16301
 18.000    6.91804E-02   0.17302       9.72438E-02   1.72746E-02
 18.000    1.75732E-02   9.63396E-04   3.9638

 20.000    9.54483E-03   9.52946E-02   0.27485       0.23047
 20.000    4.51859E-02   0.22939       0.25515       4.26459E-02
 20.000    8.41757E-02   8.29523E-03   2.9542
```

22.000	1.23431E-03	2.42505E-02	0.13398	0.20948
22.000	2.02261E-02	0.19203	0.38907	6.00564E-02
22.000	0.21111	3.35638E-02	2.1404	
24.000	3.12754E-04	8.90786E-03	7.20209E-02	0.16539
24.000	1.04069E-02	0.14422	0.42637	6.23458E-02
24.000	0.31696	6.80690E-02	1.6803	
26.000	2.22867E-04	6.76462E-03	5.91036E-02	0.14862
26.000	8.64723E-03	0.13051	0.42518	6.22657E-02
26.000	0.35044	8.32356E-02	1.5499	
28.000	2.17679E-04	6.61668E-03	5.79792E-02	0.14646
28.000	8.53957E-03	0.12942	0.42410	6.24631E-02
28.000	0.35402	8.51909E-02	1.5362	
30.000	2.17409E-04	6.60690E-03	5.78845E-02	0.14621
30.000	8.53610E-03	0.12937	0.42392	6.25138E-02
30.000	0.35435	8.53948E-02	1.5350	
32.000	2.17402E-04	6.60631E-03	5.78762E-02	0.14618
32.000	8.53647E-03	0.12936	0.42390	6.25225E-02
32.000	0.35439	8.54159E-02	1.5348	
34.000	2.17403E-04	6.60628E-03	5.78754E-02	0.14618
34.000	8.53658E-03	0.12937	0.42389	6.25239E-02
34.000	0.35439	8.54181E-02	1.5348	
36.000	2.17403E-04	6.60628E-03	5.78753E-02	0.14618
36.000	8.53660E-03	0.12937	0.42389	6.25240E-02
36.000	0.35439	8.54184E-02	1.5348	
38.000	2.17403E-04	6.60628E-03	5.78753E-02	0.14618
38.000	8.53660E-03	0.12937	0.42389	6.25241E-02
38.000	0.35439	8.54184E-02	1.5348	
40.000	2.17403E-04	6.60628E-03	5.78753E-02	0.14618
40.000	8.53661E-03	0.12937	0.42389	6.25241E-02
40.000	0.35439	8.54184E-02	1.5348	

A5.6 Program for optimising the parameter β_3 or k

```
      REAL B1,B2,B3,A,B,T1,T2,X0,X1,X2,X3,F1,F2,Z,S,EXPM(4),MODL(4)
      INTEGER T(4)

*     DATA STATEMENT TO BE SET FOR EITHER BUTYLATION OR
*     CONDENSATION
*     EXPERIMENTAL DATA : BUTYLATION / DEHYDRATION STAGE : VP5

      DATA EXPM(1),EXPM(2),EXPM(3),EXPM(4) /0.00,8.17,8.31,8.36/

      PRINT
      PRINT
      PRINT*,"INPUT PARAMETERS B1,B2"
      READ*,B1,B2

      PRINT
      PRINT
      PRINT*,"SPECIFY INTERVAL A,B TO SEARCH B3"
      READ*,A,B

*     GOLDEN SECTION SEARCH METHOD

      PRINT
      PRINT
      T1=0.3819660113
      T2=1-T1

      X0=A
      X1=A+T1*(B-A)
      X2=A+T2*(B-A)
      X3=B

      B3=X1
      CALL FUNCTN (B1,B2,B3,EXPM,MODL,T,Z)
      F1=Z

      B3=X2
      CALL FUNCTN (B1,B2,B3,EXPM,MODL,T,Z)
      F2=Z

      PRINT*," CURRENT INTERVAL "

   20 PRINT*,X0,X3

         IF (F2.LT.F1) THEN
            S=X3-X1
            X0=X1
            X1=X2
            X2=X0+T2*S
            F1=F2
            B3=X2
            CALL FUNCTN (B1,B2,B3,EXPM,MODL,T,Z)
            F2=Z
```

```
     ELSE
       S=X2-X0
       X3=X2
       X2=X1
       X1=X0+T1*S
       F2=F1
       B3=X1
       CALL FUNCTN (B1,B2,B3,EXPM,MODL,T,Z)
       F1=Z
     ENDIF
   IF (S.GT.0.00005)GOTO 20

   PRINT
   PRINT
   PRINT*,"FINAL SOLUTION"
   PRINT*,"B3              =",X1
   PRINT*,"SUM OF SQUARE=",F1

*  SIMULATION RESULTS : BUTYLATION / DEHYDRATION STAGE : VP5
*  WHILE USING THIS PROGRAM FOR CONDESATION, CHANGE
*  BUTYL ETHER TO METHYLENE ETHER

   PRINT
   PRINT
  PRINT*,"================================================="
   PRINT*,"     TIME  BUTYL ETHER         BUTYL ETHER          "
   PRINT*,"           EXPERIMENTAL        MODEL               "
   PRINT*,"     MIN.  MOLE                MOLE                "
  PRINT*,"================================================="
   PRINT
   PRINT

   DO 10 I=1,4
     PRINT*, T(I),   EXPM(I),     MODL(I)
 10 CONTINUE

   END



   SUBROUTINE FUNCTN (B1,B2,B3,EXPM,MODL,T,Z)

   REAL B1,B2,B3,EXPM(4),MODL(4),Z
   INTEGER T(4)

   DO 10 I=1,4
     T(I)=0
     MODL(I)=0
 10 CONTINUE

   I=1
   T(I)=0

   MODL(I)=B1+B2*(1-EXP(-B3*T(I)))
   Z=(EXPM(I)-MODL(I))**2
```

```
*  SET TIME INTERVAL ACCORDING TO EXPERIMENTAL DATA

   DO
     I=I+1
     T(I)=T(I-1)+80
     MODL(I)=B1+B2*(1-EXP(-B3*T(I)))
     Z=Z+(EXPM(I)-MODL(I))**2
   UNTIL (T(I).EQ.240)

   RETURN
   END
```

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