

## CHAPTER 4

### REVIEW MODELING OF PHENOL-FORMALDEHYDE REACTION

There are some studies of modeling of the reaction between phenol with formaldehyde under acid-catalyzed conditions (Kumar et.al,1980; Kumar,1982; Frontini et.al, 1982; Mirta et.al,1984). But these modeling can not be used to describe and predict the reaction under base-catalyzed conditions because these two conditions differ in the nature of reaction kinetics and mechanism. In addition, the main assumption in these studies that concentrations of mono-,di- and tri-methylolphenol are so low that can be neglected in the system is not valid for base-catalyzed conditions. On the other hand, there are few studies of the modeling of phenol and formaldehyde reaction under base-catalyzed condition due to the complicate reaction. The early investigations were mostly dealt with the kinetic studies by following the rate of disappearance of formaldehyde. Therefore in this chapter will be reviewed about the kinetic studies and also some modeling studies

of phenol and formaldehyde reaction under base-catalyzed condition.

In 1953, De Jong and his co-workers studied the kinetics of the hydroxymethylation of phenols in diluted aqueous solution, 0.1-0.4 molar, by measuring the decrease in the formaldehyde concentration. The reaction was followed to a low conversion only, in order to measure the introduction of only one methylol group and to minimise the errors due to further reaction of the products, eg., the formation of dimethylolphenol and dihydroxyphenylmethanes. The rate of the decrease of formaldehyde was suggested as the following equation.

$$-d[F]/dt = k[P]^m[F]^n \quad (4-1)$$

The order of the reaction has been determined by varying the concentration of the reactants (0.1-0.2 mol/l phenol and 0.2-0.4 mol/l formaldehyde, pH=8.0, Temp.=90 °C). The studies found that the rate is first order with respect to phenol and formaldehyde concentration (n=m=1).

Later in 1956 and 1957, these reserchers progressed their studies as the same manner as the

previous study. The reactions of phenol and formaldehyde are carried out under the temperature of 90 and 30 °C respectively and pH greater than 7. Concentration of phenol and formaldehyde is 0.1 mol/l and 0.4-0.6 mol/l. The concentration of the reactants and the reaction time were chosen in such a way that only mono-methylolphenols were formed. The reaction was followed up to a small conversion, 10 % calculated on formaldehyde. So the formation of dimethylolphenols was neglected in these studies. From the studies found that the reaction between phenol and formaldehyde in aqueous solution at 30 and 90 °C and pH about 7-10 and P:F ratio about 4-6 , approximately 58% ortho substitution and 42% para substitution takes place initially. Moreover, the results showed that the degree of ortho substitution  $[o]/[o]+[p]$  is independent of the reaction time.

In 1959, Yeddanapalli and et.al. studied the kinetics of o- and p- methylolphenol formation from phenol and formaldehyde under alkaline condition. In this study, the excess phenol concentration were used to avoid di- and tri-methylolphenol formation. NaOH was used as the catalyst. Concentration of phenol was varied from 0.2 to 1 mol/l and concentration of formaldehyde was 0.2 mol/l. The reaction temperature was varied from 60-90

°C. The study followed the reaction just the only mono-methylolphenol were formed and the reaction was stop when di-methylolphenols were formed. The rate of the reaction was found as the following equation. They suggested that rate of formaldehyde disappearance was first order with respect to formaldehyde concentration and phenate ion concentration. The overall reaction was 2nd order. The activation energy of the second-order rate constant was 19.84 kcal/mole.

$$-d[F]/dt = k[F][P^-] \quad (4-2)$$

In the same year ,they furthered their study by conducting with equimolar concentrations of phenol and formaldehyde to give, depending on temperature and time of reaction, the mono-,di-,tri-methylol phenols. The paper chromatographic technique was used to analyze the various products obtained with time and at 60,70 and 80°C. These researchers can not develop a comprehensive rate expression to cover the overall of the various methylol phenol formations. They just suggested the overall rate of disappearance of formaldehyde which was not correct under these conditions.

In 1959, Peer studied the kinetic of the first step in the reaction of phenol and formaldehyde, the formation of ortho- and para-hydroxymethylphenols under the temperature of 90 °C and pH about 8.5-10.5. In this study, the P/F ratio >10 were used to ensure that there were only o- and p-methylolphenol formation. They suggested rate equation of reaction as the following:

$$V = k' [p^-] [F_{tot}] \quad (4-3)$$

$$[P_{tot}] = [P] + [P^-] \quad (4-4)$$

$$K_p = [P^-] / [P] [OH^-] \quad (4-5)$$

where  $[P^-]$  = concentration of dissociated phenol (mol/l)  
after t sec

$[F_{tot}]$  = formaldehyde concentration (mol/l) after t sec

$[P]$  = concentration of undissociated phenol

$[P_{tot}]$  = total concentration of phenol

$[OH^-]$  = calculated  $OH^-$  ion concentration

$K_p$  = equilibrium constant of phenol equilibrium

From the study found that these equations can be used for the molar ratio  $[NaOH]/[Phenolo] < 1$ , if this ratio >1, formaldehyde is only partly converted into ortho- and para-methylolphenol due to the simultaneous occurrence of a Cannizzaro reaction at high pH.

In 1962, Dijkstra and et.al. re-investigated the hydroxymethylation of phenol in the pH range 8.5-12.5 at 30 °C in dilute aqueous solutions. They suggested rate equation of this reaction as the following:

$$V = 6.9 \times 10^{-5} [P^-] [F] [p] / 0.006 + [P] \quad \text{gmole/l-sec (4-6)}$$

This equation can be used in the range of the conditions they studied.

From the studies of these researchers, they just suggested the overall rate of disappearance of formaldehyde which is not correct under these conditions, because formaldehyde is removed from the system not only by reaction with phenol but also with the intermediate methylolphenols; in addition, at high pH, side reactions, such as self-condensation and Cannizzaro, also remove formaldehyde. Moreover, their studies just followed the reaction for only a few percent conversion. Thus no one can develop a comprehensive rate expression to cover the overall of the various methylolphenol formation. The rate equations they suggested cannot be used for describing concentrated systems, where the concentration of formaldehyde is greater than 1 molar (3 w%).



Kinetic Model by A.A. Zavitsas

Zavitsas suggested seven simultaneous reactions occurred in phenol-formaldehyde system under base-catalyzed condition according to Eq. (4-7)-(4-13). The kinetics of these reactions were described mathematically by seven simultaneous differential equations as written in Eq.(4-14)-(4-20) which describe the appearance and disappearance of each component in the system as a function of time. In addition, six simultaneous algebraic expressions were proposed for describing the distribution of ionic forms among the different phenolic components according to Eq.(4-21)-(4-26).

where  $A_1$  = phenol

$A_2$  = o-hydroxymethylphenol (o-HMP)

$A_3$  = p-hydroxymethylphenol (p-HMP)

$A_4$  = o,o-hydroxymethylphenol (o,o-DHMP)

$A_5$  = o,p-hydroxymethylphenol (o,p-DHMP)

$A_6$  = o,o,p-hydroxymethylphenol (o,o,p-THMP)

$A_i^-$  = the corresponding anion

F = formaldehyde

$\text{CH}_2\text{OHCH}_2$  = formaldehyde in form of methylene glycol



### Rate Equation

$$-d[A_1]/dt = k_1[A_1^-]m[F] + k_2[A_1^-]m[F] \quad (4-14)$$

$$-d[A_2]/dt = k_1[A_1^-]m[F] - k_3[A_2^-]m[F] - k_4[A_2^-]m[F] \quad (4-15)$$

$$-d[A_3]/dt = k_2[A_1^-]m[F] - k_5[A_3^-]m[F] \quad (4-16)$$

$$-d[A_4]/dt = k_3[A_2^-]m[F] - k_6[A_4^-]m[F] \quad (4-17)$$

$$-d[A_5]/dt = k_4[A_2^-]m[F] + k_5[A_3^-]m[F] - k_7[A_5^-]m[F] \quad (4-18)$$

$$-d[A_6]/dt = k_6[A_4^-]m[F] + k_7[A_5^-]m[F] \quad (4-19)$$

$$-d[F]/dt = m[F] (k_1[A_1^-] + k_2[A_1^-] + k_3[A_2^-] + k_4[A_2^-] + k_6[A_4^-] + k_7[A_5^-] + k_5[A_3^-]) \quad (4-20)$$



Relationships between non-ionized and ionized of phenol molecule and other methylolphenol are shown according to eq.21-26.

$$[A_1^-] + [A_2^-] + [A_3^-] + [A_4^-] + [A_5^-] + [A_6^-] = [Na^+] \quad (4-21)$$

$$[A_2^-] / [A_1^-] = K_2 ([A_2] - [A_2^-]) / K_1 ([A_1] - [A_1^-]) \quad (4-22)$$

$$[A_3^-] / [A_2^-] = K_3 ([A_3] - [A_3^-]) / K_2 ([A_2] - [A_2^-]) \quad (4-23)$$

$$[A_4^-] / [A_3^-] = K_4 ([A_4] - [A_4^-]) / K_3 ([A_3] - [A_3^-]) \quad (4-24)$$

$$[A_5^-] / [A_4^-] = K_5 ([A_5] - [A_5^-]) / K_4 ([A_4] - [A_4^-]) \quad (4-25)$$

$$[A_6^-] / [A_5^-] = K_6 ([A_6] - [A_6^-]) / K_5 ([A_5] - [A_5^-]) \quad (4-26)$$

Fraction of formaldehyde in the form of methylene glycol,  $m$ , can be calculated as shown in eq.27

$$f(m) = 3Q_1Q_2[F]^5m^5 + (3Q_1+Q_2)[F]^3[H_2O]^2m^3 + Q_2(2[F] - 3[F]) [F]^2[H_2O]^2m^2 + [F][H_2O]^4(m-1) = 0 \quad (4-27)$$

$$[H_2O] = [H_2O]_{tot} - m[F] - (1/3)(1-m)[F] \quad (4-28)$$

where  $Q_1$  and  $Q_2 = 45$  and  $400$  respectively

$m$  = fraction of formaldehyde in the form of methyleneglycol

They conducted an experimental set using phenol and formaldehyde as the reactants under base conditions. The reactions were carried out under temperature of 30

and 57 °C. In each temperature, the reactions were conducted at high and low reactant concentrations, approximately 4 and 1 molar of phenol respectively. The P:F ratio were 2 and NaOH was used as the catalyst. All products formed, mono-, di- and tri-methylolphenol, were measured during the reaction. The concentrations of all components in the system were used as the datas for estimating parameters. The above equations were solved for  $k_1-k_7$ , the rate constants of the seven hydroxymethylation reactions, by a relatively straightforward manner on a computer. The algebraic equations were substituted into the differential equations and the appearance and disappearance of the several components was simulated accordingly. The  $k_1-k_7$  value were manipulated until the simulated curves matched the experimental points. The rate constants of high concentration obtained were higher than low concentration. From the study, there is no attempt to suggest the relationship of the reactant concentration and rate constants.

In 1981, Pal et al. derived a statistical model for the formation of resols. However, this model is too complicate to describe the resols formation. The kinetic approach is a very rough approximation and the kinetic

parameters were taken from the novolac chemistry which differs widely in the nature of reactions, reactivity ratios, and substitution effects.

