

Development of A Kinetic Model for Resole Type Phenolic Resin Formation

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Abstract

A kinetic model was developed to predict the behavior of resole type phenolic resin formation under NaOH-catalyzed condition in a batch reactor. The proposed model was developed by reducing the ionization equilibrium equation for each component of Zavitsas' model and adding an equation for calculating the initial water concentration. Parameters in the proposed models were estimated and compared with experimental data from literature, in the temperature range of 30 to 70 °C and on initial phenol concentration of 0.05 to 5.375 mole/l using the simplex method. Rate constants in concentrated systems were found to be higher than those in dilute systems due to the influence of solvent quantity on rate constants. The relationship between rate constant and initial water concentration were proposed to be linear. The results show that the proposed model with the linear relationship of rate constants and initial water concentration can predict all the main components in resole resin formation.

Keywords: Modeling, Phenolic resins, Resole resins, Phenol-formaldehyde resins, Kinetic model

1. Introduction

Phenolic resins are one of the most important thermosetting polymers because of their good temperature and electrical resistance properties. Their importance is likely to remain considerable because the raw materials used can be obtained at a reasonable cost. The industrial development of phenolic resins is still continuing despite their long history.

Phenolic resins are synthesized by the reaction of phenol (P) and formaldehyde (F). Different reaction conditions result in different structures and characteristics of the products. In acidic solution, with the mole ratio of phenol to formaldehyde (P:F) larger than 1, the products are relatively linear molecular structures called novolac resins, whereas under base-catalyzed conditions with P:F ratio less than 1, short and highly methylolate structures are produced, called resole resins. Resole resins have been used in many industries since they can be crosslinked to give thermoset plastics with desirable properties without any hardening agent. Even though resole resin formation is one of the oldest known reactions, it is still difficult to describe and predict the kinetic reaction and

structures of these resins due to the complex mixture of products formed during the reactions. Earlier studies on kinetics of the reaction were mostly concerned with the overall rate of disappearance of formaldehyde or phenol concentrations [1-5]. The studies simply followed the reaction over only a few percentage of conversion and maintained the condition for only mono-methylphenols to occur. The limitation of these simplified kinetic models is that they can be used only within the specified conditions and can not be used for different conditions, because formaldehyde is removed from the system not only by the reaction with phenol, but also with the intermediate methylolphenols.

Few complete experimental studies were carried out to study the reaction of phenol with formaldehyde under a NaOH catalyzed condition according to the reaction scheme shown in Figure 1 [6,7,8]. Seven different rate constants were determined. All components in the reaction were measured. Each individual reaction has been assumed to be of first order with respect to each reaction component, formaldehyde, and phenolic anion. These rate

constants can only be used for the same condition only.

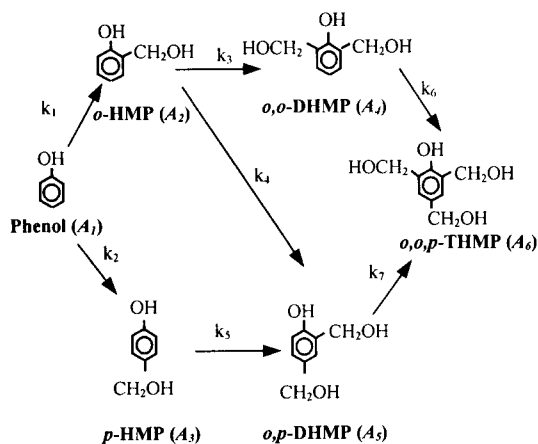


Figure 1. Reaction network of resol formation.

Zavitsas [9] suggested seven simultaneous differential equations to 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 the ionic form among the different phenolic components. Zavitsas conducted an experiment at the temperature of 30 and 57 °C. In each temperature, the reactions were conducted at high and low concentrations, i.e. approximately 4 and 1 molar of phenol respectively. The P:F ratio was 2 and NaOH was used as the catalyst. All components, phenol, formaldehyde, mono hydroxymethylolphenol (HMP), di-HMP (DHMP) and tri-HMP (THMP) were measured during the reaction and were used as the data for estimating the parameter rate constants of each reaction. Rate constants of reaction in different concentration were reported individually. The limitation of these studies is that each rate constant was obtained separately for the two concentrations. There was no suggestion of the relationship between the rate constant and the reactant concentration.

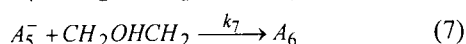
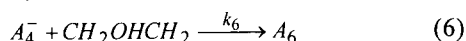
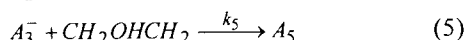
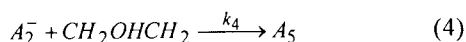
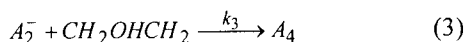
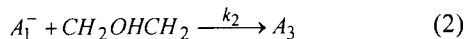
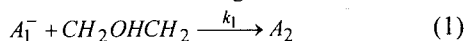
The purpose of any kinetic study is to determine how a reaction proceeds. However, the determination of reliable kinetic data for phenolic resin formation is complicated because the reaction conditions, including temperature, type and amount of catalyst, and mole ratios of reactants affect the resulting products. The identification of the reaction products is also

relatively difficult. Therefore, it is not surprising that the reported kinetic data differ considerably.

The aim of this study is to develop the kinetic model of phenol and formaldehyde reaction under base-catalyzed condition that can predict the behavior of resol resin formation in a batch reactor by using all experimental data obtained in the literature for estimating parameters in the model. The models are developed from the kinetic model obtained from Zavitsas [9].

2. Proposed Model

Seven simultaneous reactions of resol formation suggested by Zavitsas are shown in equation (1)-(7) according to the network of resol formation in Figure 1.



where A_i^- is the corresponding anion, CH_2OHCH_2 is formaldehyde in the form of methylene glycol.

2.1 Rate Equation

The kinetics of the above reactions were described mathematically by seven simultaneous differential equations as the following.

$$-d[A_1]/dt = k_1[A_1^-]m[F] + k_2[A_1^-]m[F] \quad (8)$$

$$-d[A_2]/dt = k_1[A_1^-]m[F] - k_3[A_2^-]m[F] - k_4[A_2^-]m[F] \quad (9)$$

$$-d[A_3]/dt = k_2[A_1^-]m[F] - k_5[A_3^-]m[F] \quad (10)$$

$$-d[A_4]/dt = k_3[A_2^-]m[F] - k_6[A_4^-]m[F] \quad (11)$$

$$-d[A_5]/dt = k_4[A_2^-]m[F] + k_5[A_3^-]m[F] - k_7[A_5^-]m[F] \quad (12)$$

$$-d[A_6]/dt = k_6[A_4^-]m[F] + k_7[A_5^-]m[F] \quad (13)$$

$$-d[F]/dt = m[F](k_1[A_1^-] + k_2[A_1^-] + k_3[A_2^-] + k_4[A_2^-] + k_5[A_3^-] + k_6[A_4^-] + k_7[A_5^-]) \quad (14)$$

The fraction of formaldehyde in the form of methylene glycol (m) can be calculated as follows:

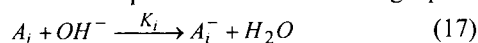
$$f(m) = 3Q_1Q_2[F]^5m^5 + (3Q_1 + Q_2)[f]^3[H_2O]^2m^3 + Q_2(2[F]_0^3[F])[F]^2[H_2O]^2m^2 + [F][H_2O]^4(m-1) = 0 \quad (15)$$

$$[H_2O] = [H_2O]_0 - m[F] - (1/3)(1-m)[F] \quad (16)$$

where Q_1 and $Q_2 = 45$ and 400 respectively [9].

2.2 Equilibrium Term Reduction

Each phenolic ion is in equilibrium with its neutral component as in the following equation.



where K_i is equilibrium constant of each component. The equilibrium equation can be written as follows:

$$K_i = \frac{A_i^-}{([A_i] - [A_i^-])[OH^-]} \quad (18)$$

K_i are found so small that A_i^- are very small when compared with A_i , [9,10]. The term $[A_i - A_i^-]$ can be assumed to be equal to $[A_i]$ to the yield

$$K_i = \frac{A_i^-}{[A_i][OH^-]} \quad (19)$$

So, the simultaneous algebraic expression of 6 phenolic ion can be calculated as the follows.

$$A_i^- = \frac{K_i}{K_1} \frac{A_i}{A_1} A_1^- \quad (18)$$

$$\text{where } \sum A_i^- = [NaOH] \quad (20)$$

The equilibrium constant of each phenolic species (K_i) at each temperature can be calculated from the relationship between temperature and equilibrium constant determined by Zavitsas[11].

Initial water concentration can be predicted from the initial reactant concentrations from the assumption that phenol and formaldehyde mixture in water does not change the density of water.

$$[H_2O]_0 = (1000 - (M_P[P]_0 + M_F[F]_0 + M_{NaOH}[NaOH]_0)) / 18 \quad (21)$$

where M_P , M_F and M_{NaOH} are molecular weight of P, F and NaOH respectively.

3. Result and Discussion

3.1 Parameter Estimation

The seven rate constants were parameters estimated by downhill simplex method and were compared with the experimental data in literature [6,9,10,12]. The results were obtained with an average sum of squares error of 0.09. All rate constants are shown in Table 1. The activation energy for both the diluted and the concentrated reactants were calculated from Arrhenius equation and are shown in Table 2.

Table 1 Rate Constants at various conditions

Temperature	30	57	30	57	30
$[P]_0$	1.003	0.9583	4.71 0	4.680	1.804
$[F]_0$	2.119	2.030	9.189	9.456	5.940
$[NaOH]_0$	0.0314	0.0125	0.0937	0.0962	1.804
k_1	.0023	0.0306	0.0064	0.1322	0.0039
k_2	.0017	0.0234	0.0039	0.0702	0.0028
k_3	.0029	0.0297	0.0062	0.0967	0.0045
k_4	.0021	0.0216	0.0056	0.0731	0.0038
k_5	.0025	0.0335	0.0056	0.0962	0.0040
k_6	.0062	0.0647	0.0113	0.1431	0.0084
k_7	.0015	0.0160	0.0045	0.0603	0.0030

Temperature is in °C.

Concentration is in mol/l, k is in l/mol-min.

Table 2 Activation Parameters

Rate Constant	Dilute System		Concentrate System	
	Ea,(kcal)	Ln A	Ea,(kcal)	ln A
k_1	19.0	25.45	22.3	31.96
k_2	19.5	26.01	21.3	29.78
k_3	17.14	22.62	20.2	28.49
k_4	17.17	22.35	18.9	26.21
k_5	19.1	25.77	20.9	29.57
k_6	17.3	23.62	18.7	26.55
k_7	17.5	22.58	19.1	26.31

From Table 1, the highest rate constant is k_6 . This rate constant is the rate of the formation of *o,o,p*-THMP from *o,o*-DHMP in *p*-site. In phenol molecule, *p*-site is more reactive than *o*-site [8]. This results in the rate of formation of *o,o,p*-THMP from *o,o*-DHMP to be higher than those from the *o,p*-DHMP. k_1 is greater than k_2 though *p*-site is more reactive than *o*-site because there are two *o*-site in phenol molecule. All rate constants in the dilute system are lower than those in the concentrate system for each temperature, because this is a reaction between neutral molecules and ion molecules in polar solvent. For the reaction occurring in polar solvent, the type and the polarity of the solvents can affect the rate of the reaction between neutral and ion molecules. For highly polar solvents such as water, the large amount of solvent decreases the rate of the reaction[9]. Consequently the rate constants are lower in diluted systems.

3.2 Rate Constant and Water Concentration Relationship

As described above and from some studies of reactions between ion and neutral molecules, a large amount of highly polar solvent such as water will decrease the rate of reaction[13]. For the plots of each rate constant shown in Table 1 against the initial water concentration, the solvent used in the system at 30 °C, straight lines were found as shown in Figure 2. Therefore it is suggested that at each temperature, each of the rate constants can be adequately related to the water concentration in a linear form as follows:

$$k_i = a_i + b_i[H_2O]_0 \quad (22)$$

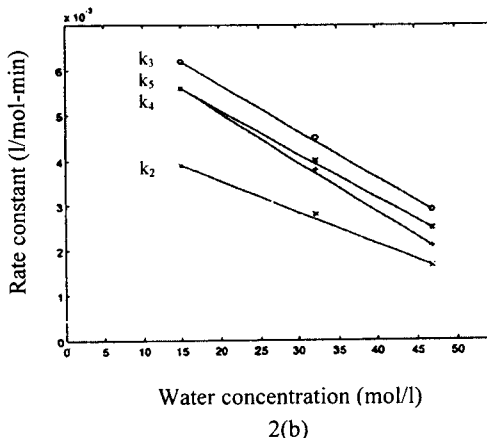
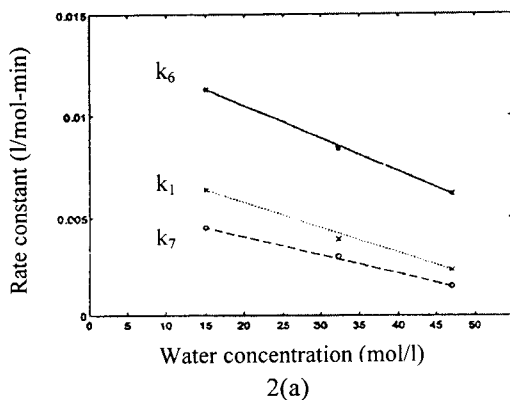


Figure 2. Water concentration and rate constants relationship at 30 °C.

3.3 Model Validation

The proposed model with the parameters obtained shown in Table 2 combined with the linear relationship of the rate constants and water concentrations were used to simulate all conditions of the experimental data in the literature. The simulation results show good agreement as illustrated in Figures 3 to 7 and Tables 3 [14].

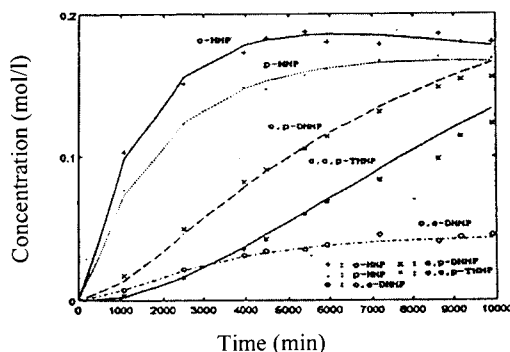


Figure 3. Product concentration at 30 °C, $[P]_0$, $[F]_0$, $[NaOH]_0 = 1.003, 2.119, 0.0314$ mol/l respectively. Point : experimental data [10], Curve: calculated.

The profiles in Figures 3 to 5 show the same manner in which the *o*-HMP concentrations are greater than those of the *p*-HMP, though the reactivity of each site is smaller than that of the *p*-HMP site, due to the presence of two *o*-sites on each phenol molecule. Thus the rate of *o*-HMP formation is greater than that of the *p*-HMP formation.

o,o-DHMP concentrations are the lowest because the rate of disappearance to form *o,o,p*-THMP is greater than the rate of formation, i.e. $k_6 > k_3$. Moreover the *p*-site in phenol molecule is more reactive than the *o*-site, this results in the rate of disappearance of *o,o*-DHMP being higher when compared with the rate of disappearance of *o,p*-DHMP.

o,p-DHMP accumulates and its amount increases as the reaction time proceeds. It is formed from both *o*-HMP and *p*-HMP at a higher rate than that of its disappearance to form *o,o,p*-HMP.

Like *o,p*-DHMP, *o,o,p*-THMP also accumulates and the amount tends to be higher because it is formed from both *o,o*-DHMP and *o,p*-DHMP.

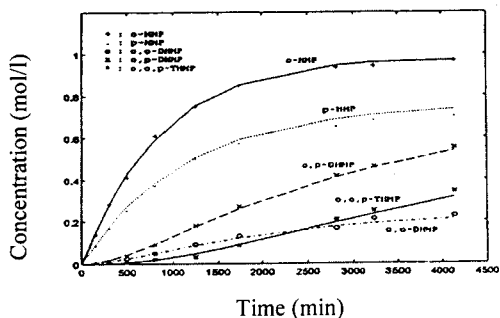


Figure 4. Product concentration at 30 °C, $[P]_0$, $[F]_0$, $[NaOH]_0 = 4.71, 9.189, 0.0937$ mol/l respectively. Point : experimental data [10], Curve: calculated.

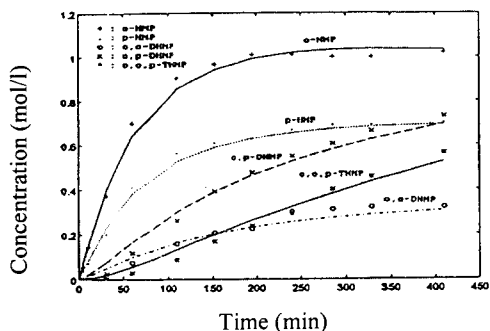


Figure 5. Product concentration at 57 °C, $[P]_0$, $[F]_0$, $[NaOH]_0 = 4.68, 9.46, 0.0962$ mol/l respectively. Point : experimental data [9], Curve: calculated.

Figure 6 shows that rate of formation and disappearance of each component is higher than those in Figure 3-5 because of the higher mole ratio of P:F and also higher catalyst concentration.

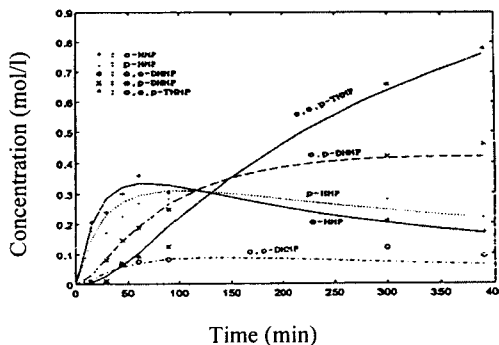


Figure 6. Product concentration at 30 °C, $[P]_0$, $[F]_0$, $[NaOH]_0 = 1.84, 5.94, 1.84$ mol/l respectively. Point : experimental data [6], Curve: calculated.

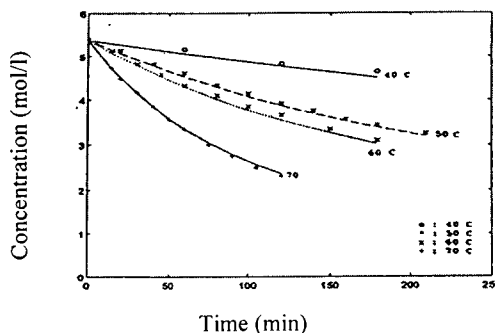


Figure 7. Formaldehyde concentration at various temperatures. $[P]_0$, $[F]_0 = 5.375$ and 5.375 mol/l

Point: experimental data [12], Curve: calculated

- Temperature = 40 °C : $[NaOH]_0 = 0.1$ mol/l
- Temperature = 50 °C : $[NaOH]_0 = 0.1$ mol/l
- Temperature = 60 °C : $[NaOH]_0 = 0.05$ mol/l
- Temperature = 70 °C : $[NaOH]_0 = 0.05$ mol/l

Figure 7 compares the calculated concentration of formaldehyde with the experimental data at various temperatures. Both sets of results are in good agreement. They also show the effect of temperature and base concentration on the rate of reaction. The rate of reactions at a higher reaction temperature are greater than those at the lower temperature.

Table 3 shows the validity of the model in the prediction of all components in the reaction carried out at 45 °C after the reaction time of 5 and 20 hours when compared with the experimental data [9].

Table 3. Simulation results compared with experimental results [9]

Products	Concentration (mol/l)			
	T = 5 hours		T = 20 hours	
	Exp.	Cal.	Exp.	Cal.
<i>o</i> -HMP	0.775	0.832	0.919	0.96
<i>p</i> -HMP	0.525	0.531	0.7	0.69
<i>o,o</i> -HMP	0.130	0.127	0.294	0.27
<i>o,p</i> -DHMP	0.237	0.243	0.66	0.67
<i>o,o,p</i> -DHMP	0.075	0.087	0.53	0.50

T = reaction time, Exp. = Experiment, Cal = Calculation, $[P]_0 = 4.42$ mol/l, $[F]_0 = 9.3$ mol/l, $[\text{NaOH}]_0 = 0.0937$ mol/l, Temperature = 45 °C.

4. Conclusions

The kinetic models of the resole type phenolic resin formation are developed for the prediction of the behavior of the phenol and formaldehyde reaction under NaOH catalysis in isothermal batch reactor. The proposed model with the linear relationship between the rate constant and water concentration can predict the behavior of resole formation when compared with all the data from literature at a temperature range from 30-70 °C and the initial phenol concentration in the range of 0.05 to 5.375 mol/l.

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6. References

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