

CHAPTER 5

MODELING AND MODEL DISCRIMINATION

As discussed in the Chapter 4, Zavitsas' model was the best model to predict the resole resin formation, but the studies were limited at 2 temperatures and no discussion about the relationship between rate constant and concentration of the reactants. Thus in this study, the new models for phenol-formaldehyde reactions are developed from Zavitsas model to predict the reaction covering all conditions from the literatures. The parameters are estimated by using the experimental data and conditions from the literature listed in the appendix B. The reactor used in this study is batch reactor. The catalyst used is NaOH which is one of the most important catalysts in the industrial production of resole resin (Knop, et.al (1985)).

Assumption

The assumptions in the development are :

- (1) The reactor is well-mixed reactor.

(2) The density and viscosity change with reaction is small and can be neglected (Zavitsas, et.al (1967,1968)).

(3) The reaction is carried out isothermally.

(4) The methylol formations are irreversible reactions.

There are 3 models considered in this study.

- (1) Simple model
- (2) Zavitsas' model
- (3) Proposed model

Simple Model

Simple model is the general model of resole formation which do not involve any equilibrium in the reactions. The reaction network for simple model are shown in Figure 5-1.

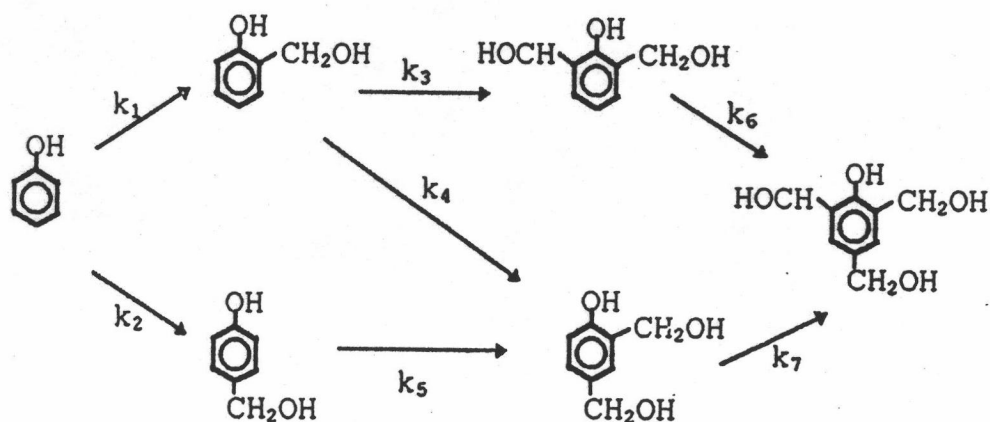


Figure 5-1 The reaction network of resole formation.

1. The kinetic model

$$-d[A_1]/dt = k_1[A_1][F] + k_2[A_1][F] \quad (5-1)$$

$$-d[A_2]/dt = k_1[A_1][F] - k_3[A_2][F] - k_4[A_2][F] \quad (5-2)$$

$$-d[A_3]/dt = k_2[A_1][F] - k_5[A_3][F] \quad (5-3)$$

$$-d[A_4]/dt = k_3[A_2][F] - k_6[A_4][F] \quad (5-4)$$

$$-d[A_5]/dt = k_4[A_2][F] + k_5[A_3][F] - k_7[A_5][F] \quad (5-5)$$

$$-d[A_6]/dt = k_6[A_4][F] + k_7[A_5][F] \quad (5-6)$$

$$-d[F]/dt = [F] \cdot (k_1[A_1] + k_2[A_1] + k_3[A_2] + k_4[A_2] + k_5[A_3] + k_6[A_4] + k_7[A_5]) \quad (5-7)$$

Rate constants, k_1 - k_7 , were estimated by comparing with experimental data from Zavitsas et.al (1966, 1967, 1968) at 30 °C and 57 °C: high reactant concentration and low concentration and from Freeman et.al (1954) at 30 °C. The parameter estimation method is downhill simplex method written in MATLAB program as discussed in Appendix A and the program shown in Appendix D.

Curves calculated with best fit are shown in Figure 5-2 and 5-3 for concentrate run at 30 °C and in Figure 5-4 and 5-5 for concentrate run at 57 °C. The rate constants obtained are listed in Table 5-1.

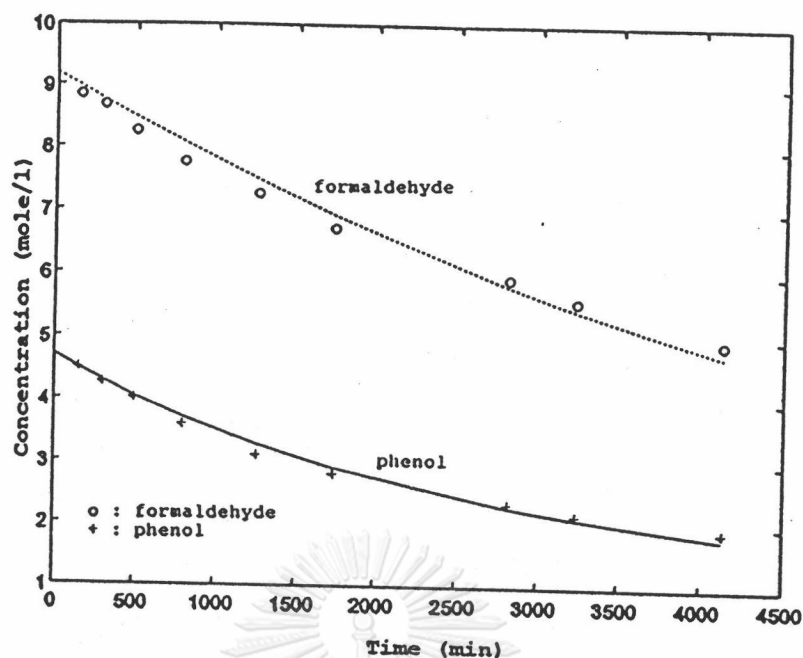


Figure 5-2 Reactant concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated with rate constants from Table 5-1 by Simple model. Point: experimental data (Zavitsas (1966)).

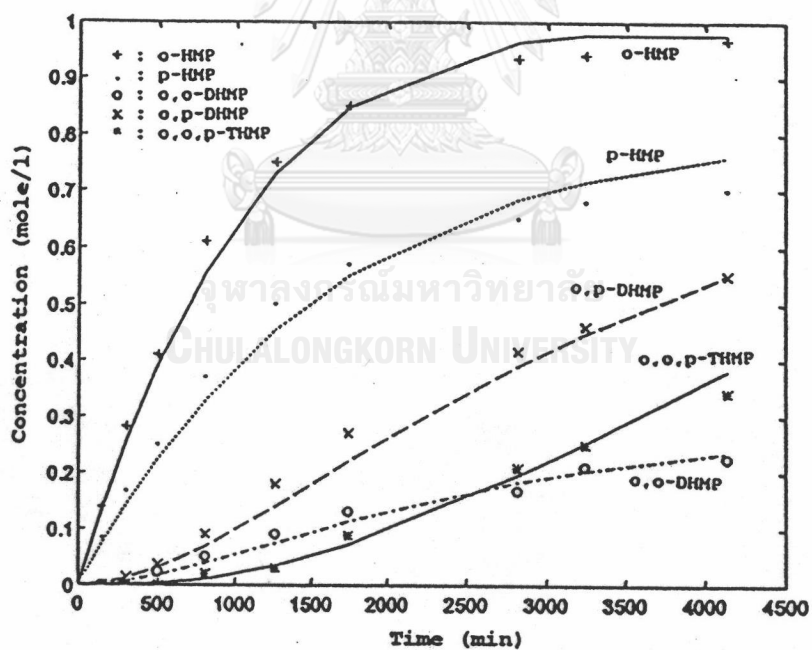


Figure 5-3 Product concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated with rate constants from Table 5-1 by Simple model. Point: experimental data (Zavitsas (1966)).

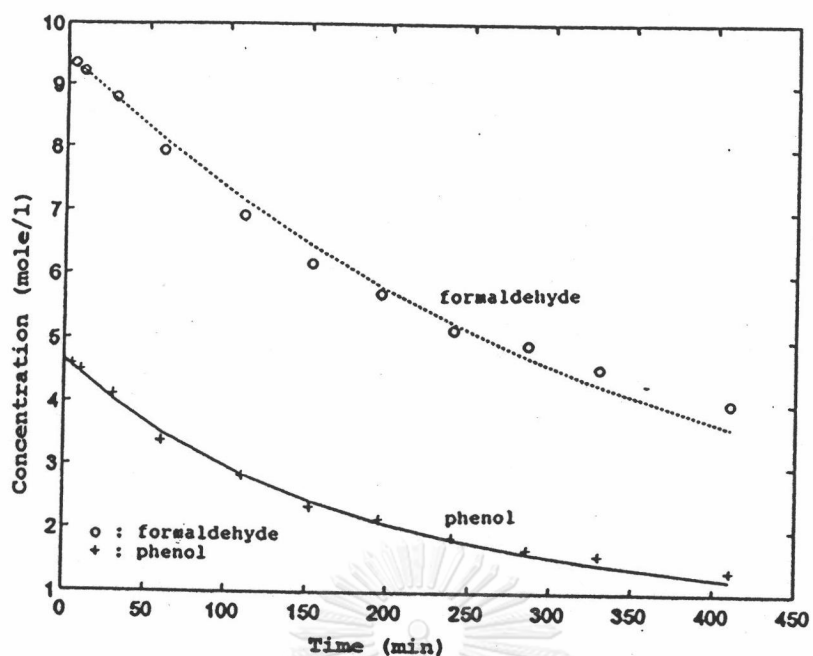


Figure 5-4 Reactant concentration vs. time at 57°C, $[P]_0=4.68$ M. $[F]_0 = 9.456$ M. $[\text{NaOH}]_0=0.09615$ M.: Curve calculated with rate constants from Table 5-1 by Simple model. Point: experimental data (Zavitsas (1966)).

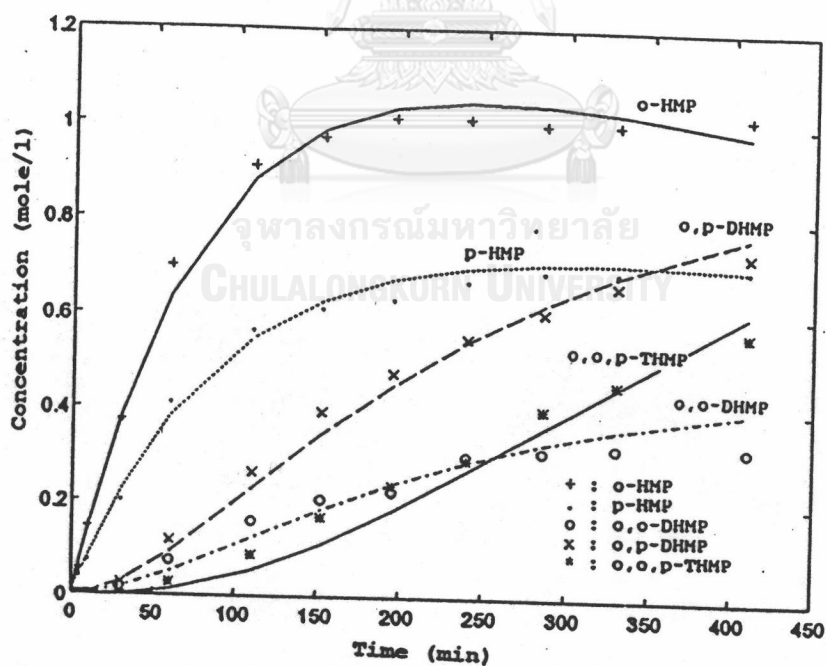


Figure 5-5 Product concentration vs. time at 57°C, $[P]_0=4.68$ M. $[F]_0 = 9.456$ M. $[\text{NaOH}]_0=0.09615$ M.: Curve calculated with rate constants from Table 5-1 by Simple model. Point: experimental data (Zavitsas (1966)).

Table 5-1 Calculated Rate Constants from Parameter Estimation from Simple Model

Temp., (°C)	30	57	30	57	30
[P] ₀ , (M.)	1.003	0.9583	4.71	4.68	1.804
[F] ₀ , (M.)	2.119	2.030	9.189	9.456	5.94
[NaOH] ₀ , (M.)	0.03138	0.0125	0.09369	0.09615	1.804
k ₁ , (l/mole.min)x10 ⁵	5.3	30	2.25	35	130
k ₂ , (l/mole.min)x10 ⁵	3.35	19	1.22	20	85
k ₃ , (l/mole.min)x10 ⁵	4.7	30	2.1	30	90
k ₄ , (l/mole.min)x10 ⁵	7.2	39	2.4	30	150
k ₅ , (l/mole.min)x10 ⁵	5.77	36	1.923	42	110
k ₆ , (l/mole.min)x10 ⁵	13	70	6	50	200
k ₇ , (l/mole.min)x10 ⁵	8	53.5	3	40	130

From the table above, rate constants at high concentration are less than at low concentrations about 2 times in both temperatures. From the studies of Yeddanapalli et.al(1959) shown that rate constants of methylol formation were related to temperature as Arrhenius relationship. Therefore, the activation energy in this study were calculated seperately in both concentration by using the Arrhenius relationship, eq.(5-8), where k₁ depicts the rate constant at the temperature

T_1 , A is the frequency factor, and E is the activation energy.

$$k_1 = Ae^{-E/RT_1} \quad (5-8)$$

The calculated activation energy are shown in Tabel 5-2.

Table 5-2 Activation Parameters for the NaOH-Catalyzed Hydroxymethylation from Simple Model

Rate Constant	Dilute Systems		Concentrate Systems	
	E_a , (kcal)	ln A	E_a , (kcal)	ln A
k_1	12.756	11.34	20.195	22.84
k_2	12.771	10.91	20.581	22.87
k_3	13.640	12.69	19.568	21.73
k_4	12.432	11.11	18.586	20.23
k_5	13.472	12.62	22.692	26.83
k_6	12.388	11.63	15.602	16.19
k_7	13.983	13.79	19.061	21.24

Zavitsas' Model

This model was used in this study to compare with Simple model and the Proposed model. The model consistes

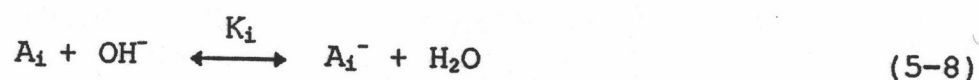
of 6 simultaneous reactions which involve the phenate ion equilibrium, formaldehyde equilibrium and hemiformal equilibrium as described in Chapter 4. Rate constants and activation energy obtained from Zavitsas according to Table C-1 and C-2 respectively in Appendix C were used to simulate the model and compared with Simple and Proposed model. The calculated curves compare with experimental data (Zavitsas (1966) are shown in Figure 5-6 and 5-7, for the others are shown in Appendix E.

Proposed Model

(1) Equilibrium Term Reduction

From Zavitsas model described in Chapter 4, the phenate ion equilibrium equations are very complex. Thus in this study, these equations had been reduced to be the easier form.

From the phenate ion equilibrium:



where A_1 = phenolic components as described in Chapter 4.

K_1 = equilibrium constant of each component



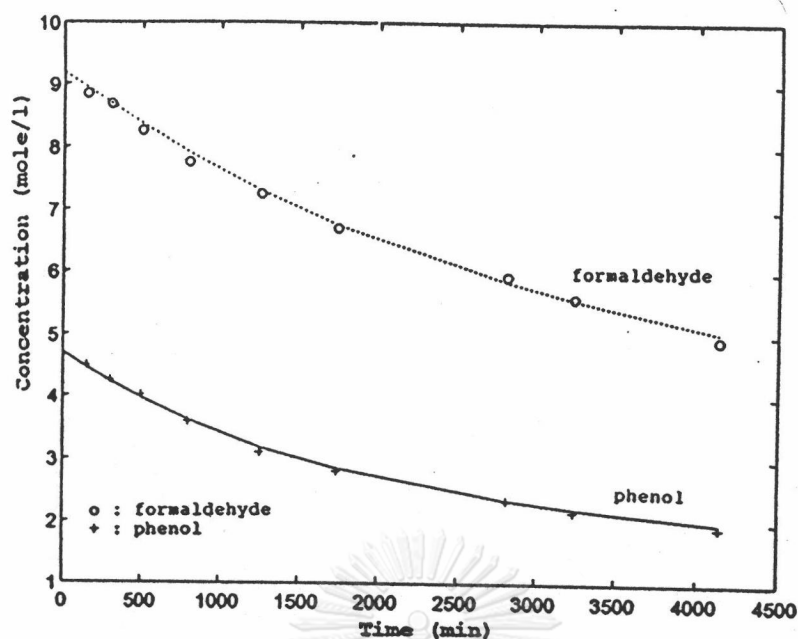


Figure 5-6 Reactant concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated with rate constants from Table C-1 by Zavitsas' model. Point: experimental data (Zavitsas (1966)).

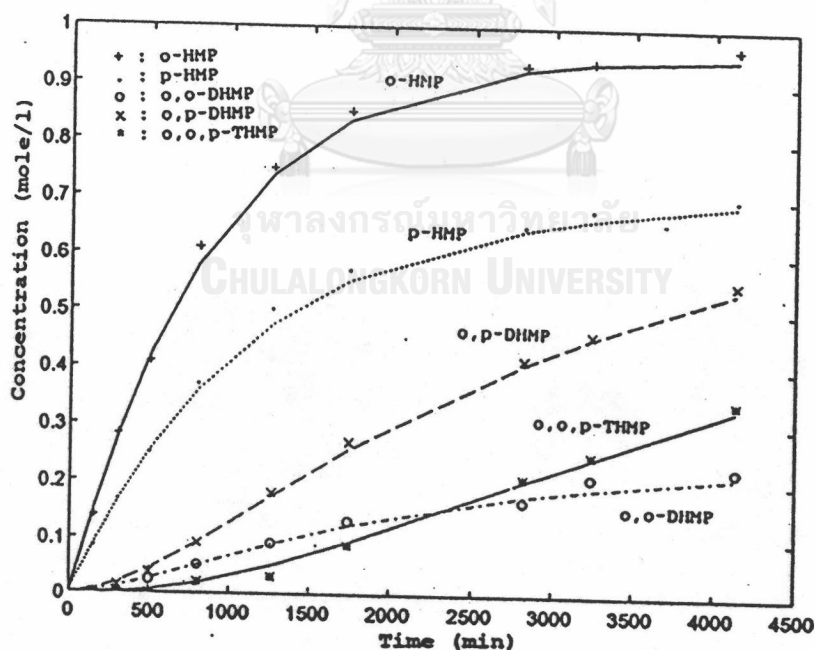


Figure 5-7 Product concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated with rate constants from Table C-1 by Zavitsas' model. Point: experimental data (Zavitsas (1966)).

Eq.(5-8) was written in equilibrium equation as the following:

$$K_1 = [A_1^-] / ([A_1] - [A_1^-]) * [OH^-] \quad (5-9)$$

From the experimental studies of Sprengling et.al(1965) and Zavitsas(1966), K_1 are so small that the A_1^- are much small when compare with A_1 . Thus the term $([A_1] - [A_1^-])$ were assumed to equal to $[A_1]$.

$$K_1 = [A_1^-] / ([A_1] [OH^-]) \quad (5-10)$$

The simultaneous algebraic expression of 6 phenate ion from Zavitsas can be written as the above form (Eq. 5-10) and rearrange to the simpler form to calculate.

$$\sum A_i^- = [NaOH] \quad (5-11)$$

$$A_i^- = (K_i/K_1) * (A_1/A_1) * A_1^- \quad (i=1-6) \quad (5-12)$$

2. Water Concentration Equation

From Zavitsas' model, the initial water concentration in the system must be input to calculate the methylene glycol fraction. In this study, the

equation for calculating initial water concentration from the initial reactant concentrations was suggested as the following equation by the assumption that phenol and formaldehyde mixture in water does not change the density of water .

$$[H_2O]_0 = (1000 - (M_{WP}[P]_0 + M_{WF}[F]_0 + M_{WNaOH}[NaOH]_0)) / 18 \quad (5-13)$$

Where M_{WP} , M_{WF} , M_{WNaOH} are molecular weights of phenol, formaldehyde and NaOH.

Eq. (5-11)-(5-13) were combined with differential equations (Eq. (4-16)-(4-20)) and equation for calculating fraction of methylene glycol of Zavitsas' model (Eq. (4-27) and (4-28)) and thus the new Proposed model are obtained.

The 7 rate constants are parameters estimated by downhill simplex method compared with experimental data of Zavitsas (1966, 1967, 1968) and Freeman (1954). Table 5-3 and 5-4 shows rate constants from parameter estimation and activation energy calculated from Arrhenius equation. The curves calculated with rate constants from Table 5-3 are shown in Figure 5-8 and 5-9 for concentrate run at 30 °C.

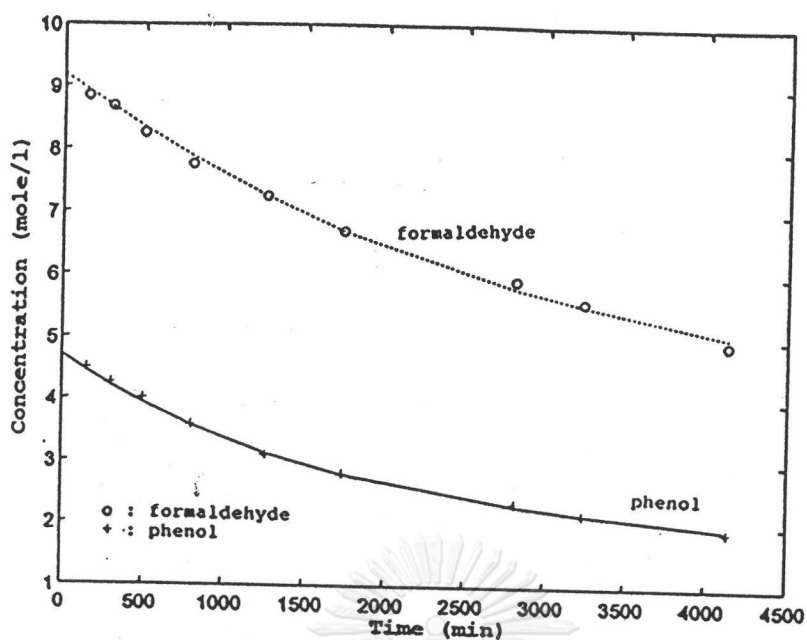


Figure 5-8 Reactant concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated with rate constants from Table 5-3 by Proposed Model. Point: experimental data (Zavitsas (1966)).

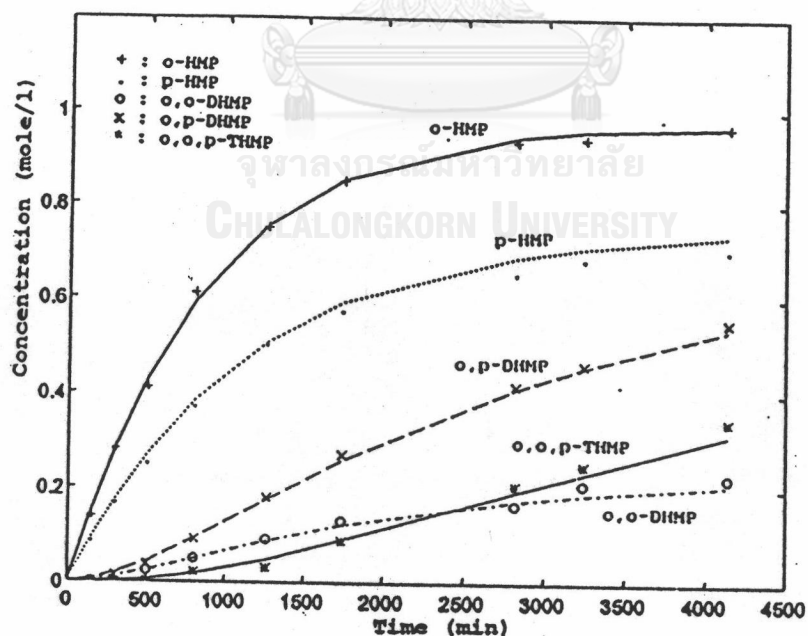


Figure 5-9 Product concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated with rate constants from Table 5-3 by Proposed Model. Point: experimental data (Zavitsas (1966)).

Table 5-3 Rate Constants Obtained from Proposed Model

Temp., (°C)	30	57	30	57	30
[P] ₀ , (M.)	1.003	0.9583	4.71	4.68	1.804
[F] ₀ , (M.)	2.119	2.030	9.189	9.456	5.94
[NaOH] ₀ , (M.)	0.03138	0.0125	0.09369	0.09615	1.804
k ₁ , (l/mole.min)	0.0023	0.0306	0.0064	0.1322	0.0039
k ₂ , (l/mole.min)	0.0017	0.0234	0.0039	0.0702	0.0028
k ₃ , (l/mole.min)	0.0029	0.0297	0.0062	0.0967	0.0045
k ₄ , (l/mole.min)	0.0021	0.0216	0.0056	0.0731	0.0038
k ₅ , (l/mole.min)	0.0025	0.0335	0.0056	0.0962	0.0040
k ₆ , (l/mole.min)	0.0062	0.0647	0.0113	0.1431	0.0084
k ₇ , (l/mole.min)	0.0015	0.0160	0.0045	0.0603	0.003

Table 5-4 Activation Parameters for the NaOH-Catalyzed Hydroxymethylation from Proposed Model

Rate Constant	Dilute Systems		Concentrate Systems	
	E _a , (kcal)	ln A	E _a , (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

Figure 5-10 and 5-11 show the comparative curves calculated with parameters from Simple model, Zavitsas' model and Proposed model. Sum of square error from estimating parameter of the 3 models are also compared as shown in table 5-5.

Table 5-5 Sum of Square Error from 3 Models.

Condition	Sum of Square Error		
	Simple Model	Zavitsas' Model	Proposed Model
30°C, dilute	0.043	0.022	0.0187
30°C, concentrate	0.431	0.102	0.086
57°C, dilute	0.0041	0.0002	0.0002
57°C, concentrate	0.5719	0.704	0.345
30°C, (Freeman)	0.26	0.21	0.30

From table 5-1 and 5-3, rate constants obtained from Simple model are much lower than from Zavitsas' and Proposed model (100 times). Because the model does not involve the equilibrium effect and the model represent the reactions between neutral and neutral molecules which are often abnormally slow (Arthur et.al(1953)). From various studies of reactions between phenol and formaldehyde under base conditions (Peer et.al(1962), Yeddanapalli et.al (1968)) shown that the reactive

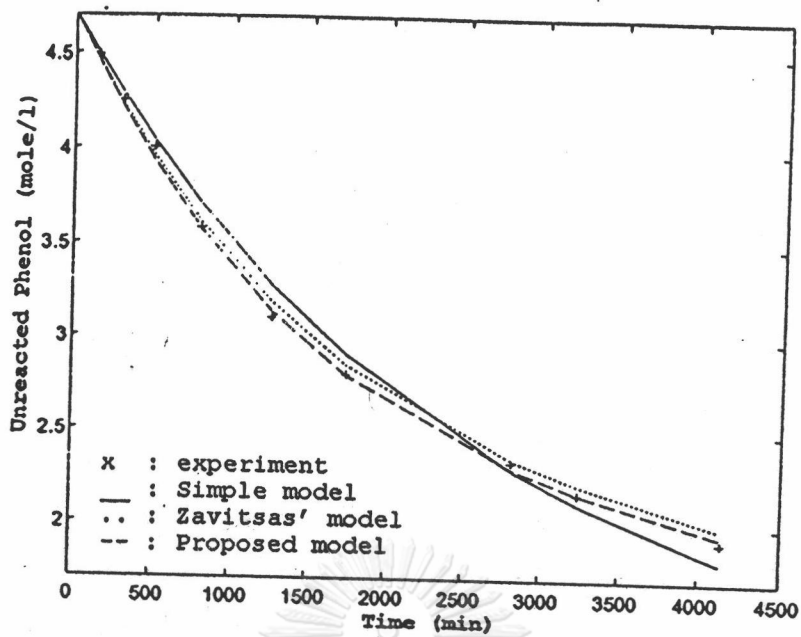


Figure 5-10 Phenol concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated compare between 3 models: Simple, Zavitsas and Proposed model. Point: experimental data (Zavitsas (1966)).

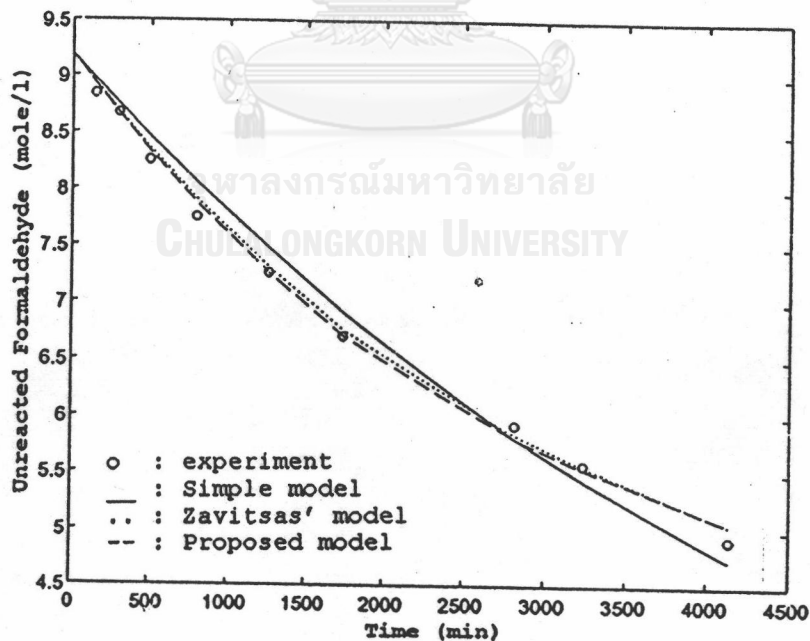


Figure 5-11 Formaldehyde concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve calculated compare between 3 models: Simple, Zavitsas and Proposed model. Point: experimental data (Zavitsas (1966)).

species are phenate ion and formaldehyde, thus this model is not the correct model to describe this system of reaction. To show that though the Simple model can be fitted with the experimental data sets from Zavitsas, the parameters obtained can not be used to predict the other conditions. Therefore it will be used comparing with Zavitsas' and Proposed model to find out the relationship between rate constants and system concentrations.

The rate constant obtained from Proposed model in dilute system are lower than in concentrate system because this is the reaction between neutral molecules and ion molecules in polar solvent. Type and polarity of solvents effect rate of reaction between neutral and ion molecules. For highly polar solvents (Arthur et.al(1953)) such as water, the large amount of solvent decrease the rate of reaction(Scatchard (1931)). Consequently rate constants are lower in dilute concentrations.

(3) Relationship between Rate Constants and Water Concentrations

From various studies of reactions between ion and neutral molecules, types and quantities of solvents effect the rate of reaction. In dilute concentration

(highly content of water), dielectric constant is higher than in concentrated concentration (lower content of water). The rate constant in a medium of lower dielectric constants is higher than in a medium of higher dielectric constant (Hughes et.al(1935) and Laidler et.al(1940)). Therefore in this study, the relationship between water concentration (amount of solvent) and rate constants were used instead of water concentration and dielectric constant. Because there is no exact equation to predict the effect of different solvent on the reaction of neutral and ion molecules(Arthur (1953)), thus in this study, two relationship between water concentration and rate constant were used to compare each other. From table 5-3, each rate constant at 30 °C was plotted against initial total water concentration according to Figure 5-12 and 5-13, the straight lines were obtained. Thus the first equation is that rate constants at each temperature relate to water concentration in linear form.

$$k_1 = a_1 + b_1[\text{H}_2\text{O}]_0 \quad (5-14)$$

The second equation was Born equation (Born (1920)) which can be written in simple form.

$$k_1 = A_1 \exp(B_1/D) \quad (5-15)$$

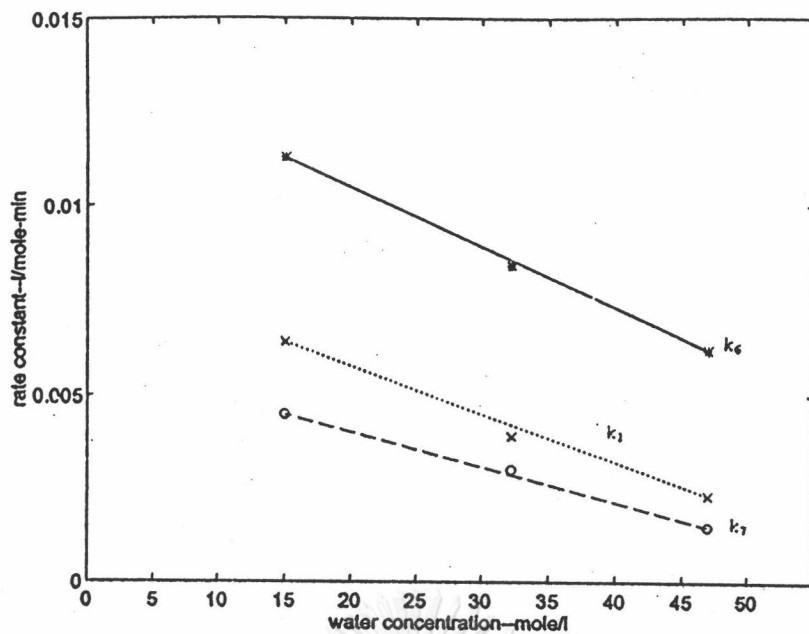


Figure 5-12 Relationship between water concentration and rate constants (for k_1 , k_6 and k_7) at 30°C. (k_1 , k_6 and k_7 refer to rate constants listed in Table 5-3)

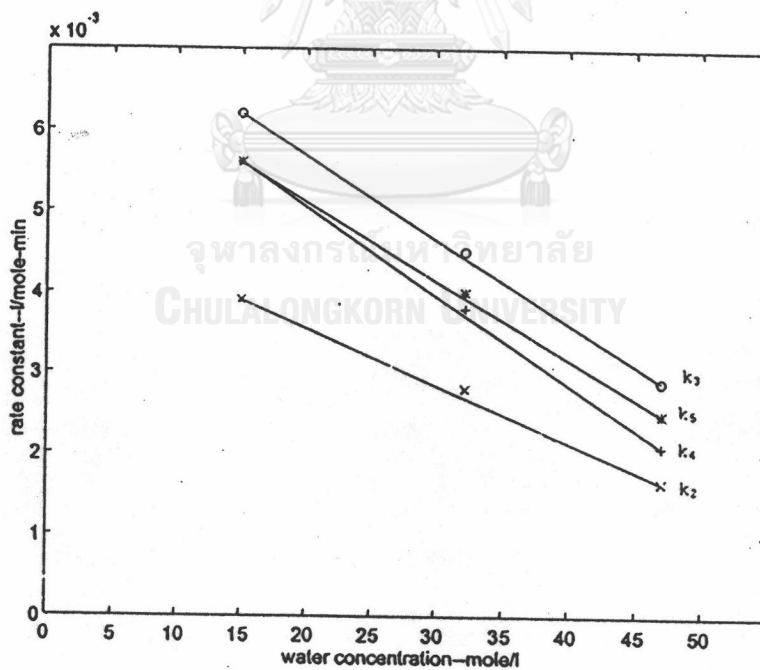


Figure 5-13 Relationship between water concentration and rate constants (for k_2 , k_3 , k_4 and k_5) at 30°C. (k_2 , k_3 , k_4 and k_5 refer to rate constants listed in Table 5-3)

where A and B are constants for each system

D is dielectric constant of the solvent

As described above water concentration is used instead of dielectric constant. Eq.(5-15) is written in the term of water concentration according to Eq.(5-16).

$$k_1 = A_1 \exp(B_1/[H_2O]_0) \quad (5-16)$$

These two relationships were substituted into the 3 models of the preceding part and 6 models are obtained.

1. Simple model with Born's relationship
2. Simple model with linear relationship
3. Zavitsas model with Born's relationship
4. Zavitsas model with linear relationship
5. Proposed model with Born's relationship
6. Proposed model with linear relationship

All the experimental datas given were used to test these models by inputting the initial conditions into the computer program, then calculate rate constants at high and low concentration by the activation energy reported in table 5-2,C-3 and 5-4 and then calculate rate constants of the experimental conditions. The simulating results from six models are plotted comparing with the

experimental datas as shown in Figure 5-14,5-15,5-16 and 5-17.

The average percent error from each model comparing with the experiments are calculated as reported in table 5-6.

Table 5-6 Average Percent Error of Each Model

Case*	Average percent error (%)					
	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
5	1.1	1.3	0.7	0.2	0.3	0.8
6	10.7	11.1	0.7	3.2	4.0	1.1
7	2.9	3.8	0.9	3.0	4.0	1.5
8	3.2	6.5	1.08	7.5	9.6	0.9
9	7.3	1.8	17.0	6.0	19.0	0.3
10	2.3	2.3	0.2	0.7	0.2	0.9
11	62.7	62.7	3.4	8.75	4.16	13.0
12	52.0	53.0	8.1	8.6	6.9	4.0
13	6.3	6.7	0.7	2.2	3.2	0.9
14	0.9	0.9	1.7	0.6	0.2	0.2
15	1.5	1.6	0.6	1.3	0.9	0.3
16	1.4	1.6	0.5	1.05	1.13	0.4
17	45.0	45.0	7.8	5.3	8.0	4.0
18	44.0	44.0	4.6	2.6	48.0	1.79
20	11.0	11.6	12.7	8.7	7.3	4.2

* Case number and condition are listed in Appendix B.

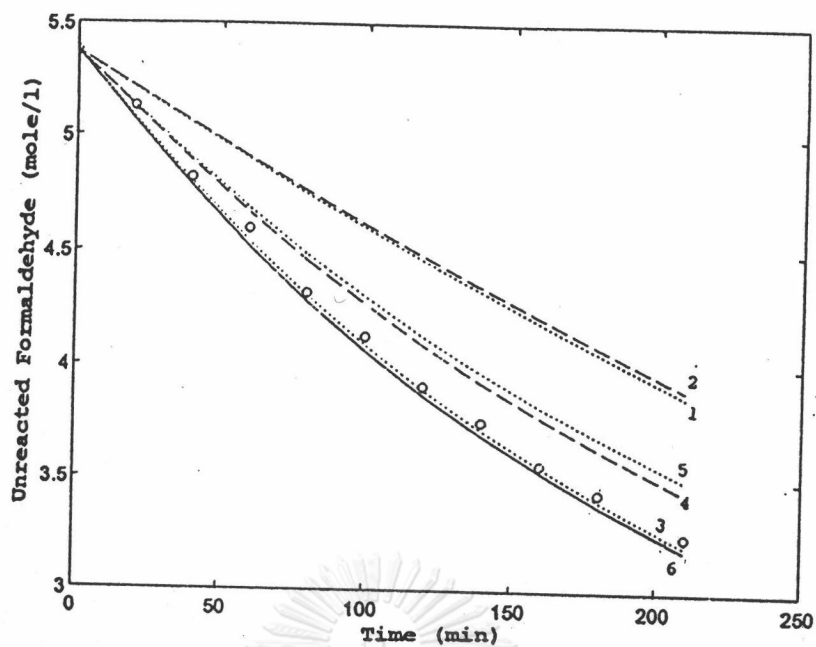


Figure 5-14 Formaldehyde concentration vs. time at 50°C, $[P]_0 = 5.375$ M. $[F]_0 = 5.375$ M. $[NaOH] = 0.1$ M.: Curve calculated compare between 6 models described in Page 58. Point: experimental data (Dejong et.al (1952)).

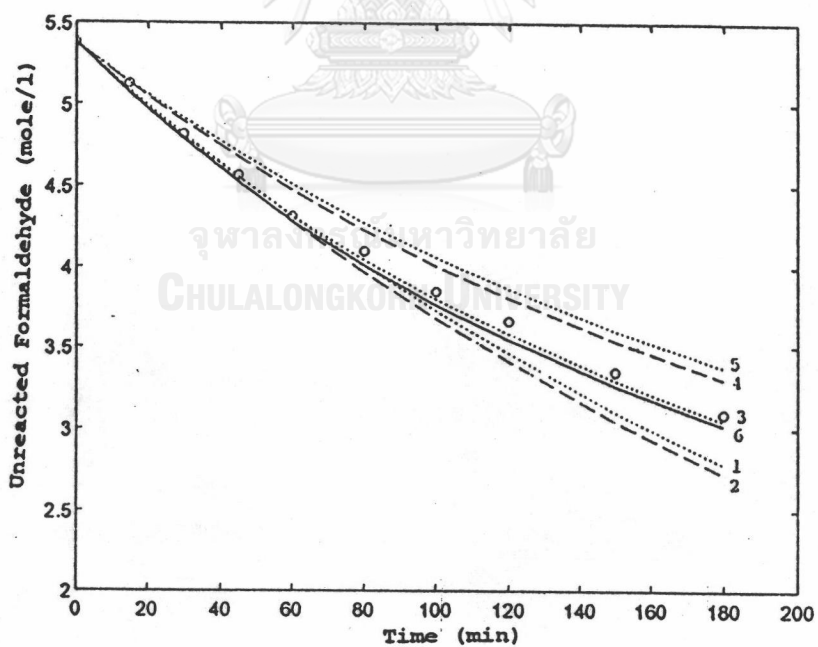


Figure 5-15 Formaldehyde concentration vs. time at 60°C, $[P]_0 = 5.375$ M. $[F]_0 = 5.375$ M. $[NaOH] = 0.05$ M.: Curve calculated compare between 6 models described in Page 58. Point: experimental data (Dejong et.al (1952)).

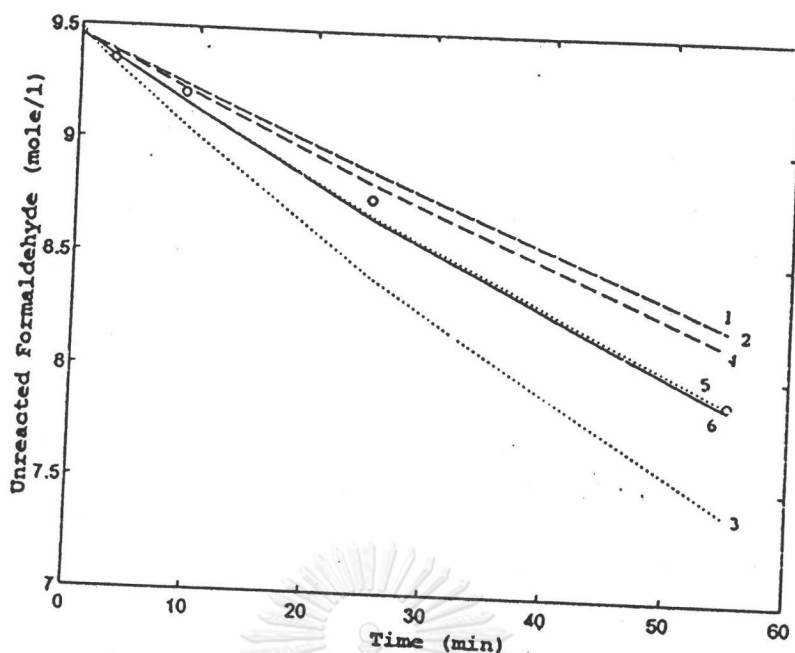


Figure 5-16 Formaldehyde concentration vs. time at 57°C, $[P]_0 = 4.68$ M. $[F]_0 = 9.46$ M. $[\text{NaOH}] = 0.095$ M.: Curve calculated compare between 6 models described in Page 58. Point: experimental data (Zavitsas et.al (1967)).

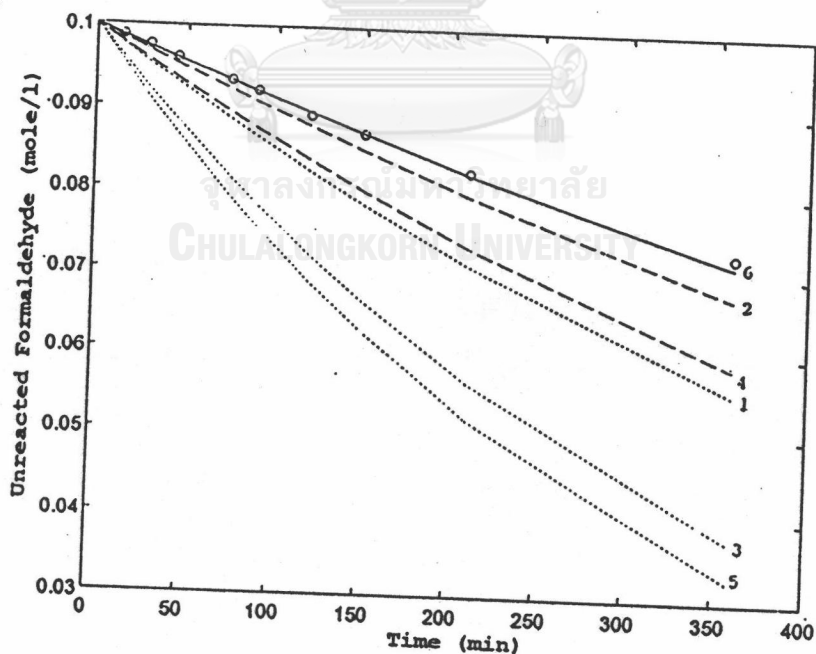


Figure 5-17 Formaldehyde concentration vs. time at 90°C, $[P]_0 = 0.6$ M. $[F]_0 = 0.1$ M. $[\text{NaOH}] = 0.0045$ M.: Curve calculated compare between 6 models described in Page 58. Point: experimental data (Dejong et.al (1956)).

From Figure 5-14 to 5-17 and the table above, though the third model which is the Zavitsas model and the Born's relationship can predict almost conditions, but in some conditions, great average percent errors are obtained. Whereas the sixth model can predicts almost all conditions.

The results indicate that eventhought Simple model can be fitted with Zavitsas' datas, the model and the parameters obtained can not be used to predict other conditions and the best model is Proposed model with the linear relationship between rate constants and water concentrations.

Simulation Results

The Proposed model with the linear relationship of rate constants and water concentrations were used to simulate all conditions of the experimental datas in each case as reported in Appendix B. The results show good agreement as shown in the following Figures and Tables.

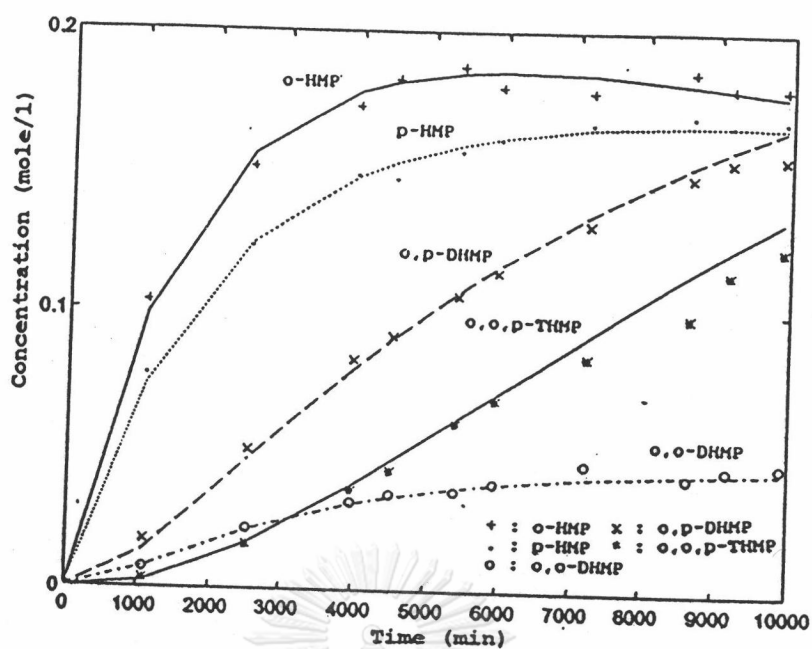


Figure 5-18 Product concentration vs. time at 30°C, $[P]_0=1.003$ M. $[F]_0 = 2.119$ M. $[\text{NaOH}]_0=0.03138$ M.: Curve: calculated. Point: experimental data (Zavitsas et.al(1968)).

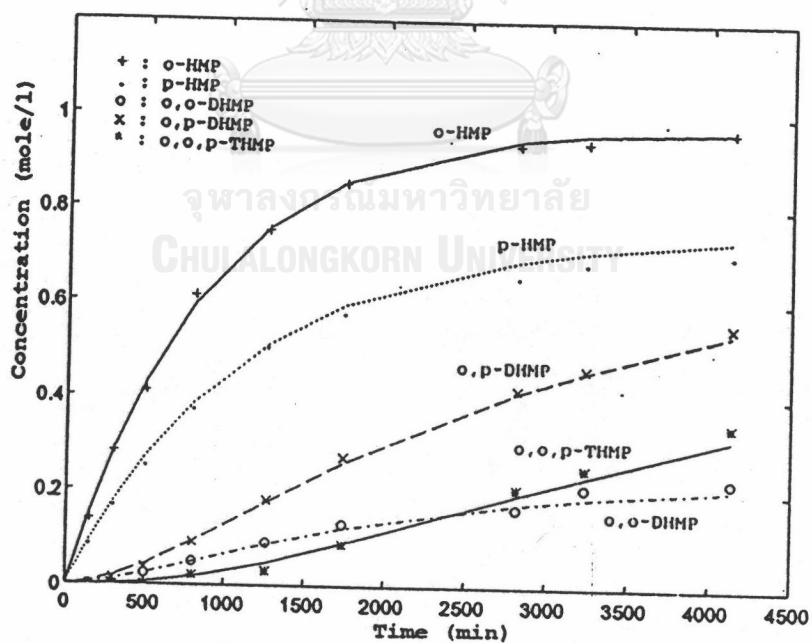


Figure 5-19 Product concentration vs. time at 30°C, $[P]_0=4.71$ M. $[F]_0 = 9.189$ M. $[\text{NaOH}]_0=0.09369$ M.: Curve: calculated. Point: experimental data (Zavitsas (1966)).

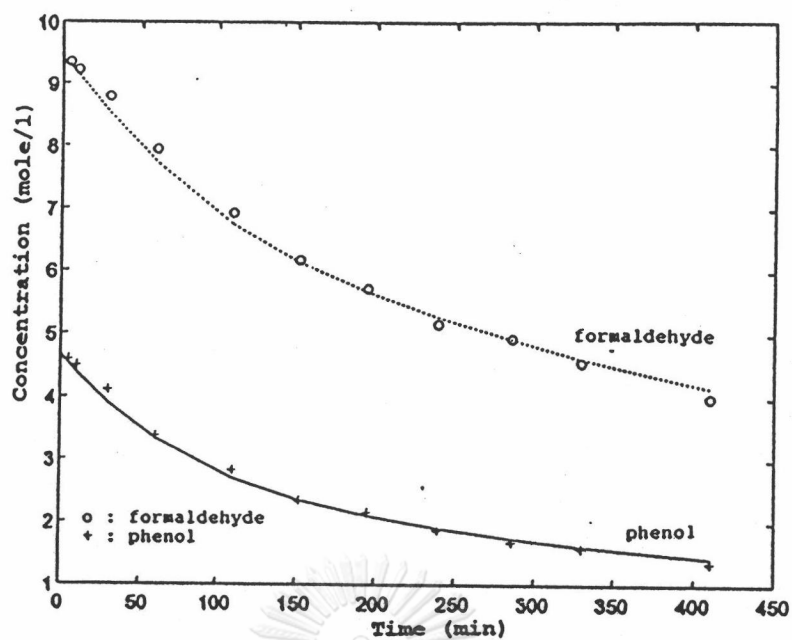


Figure 5-20 Reactant concentration vs. time at 57°C, $[P]_0=4.68$ M. $[F]_0 = 9.456$ M. $[\text{NaOH}]_0=0.09615$ M.: Curve: calculated. Point: experimental data (Zavitsas (1966)).

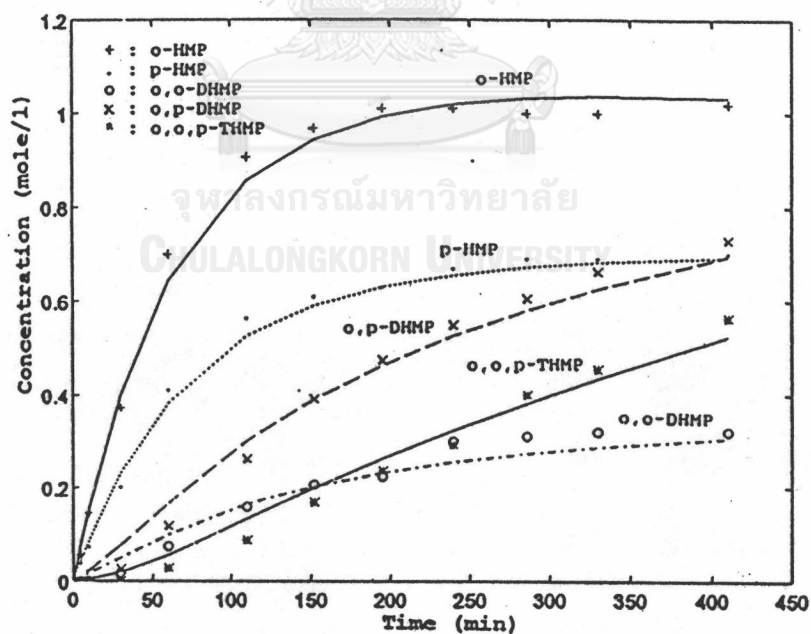


Figure 5-21 Product concentration vs. time at 57°C, $[P]_0=4.68$ M. $[F]_0 = 9.456$ M. $[\text{NaOH}]_0=0.09615$ M.: Curve : calculated. Point: experimental data (Zavitsas (1966)).

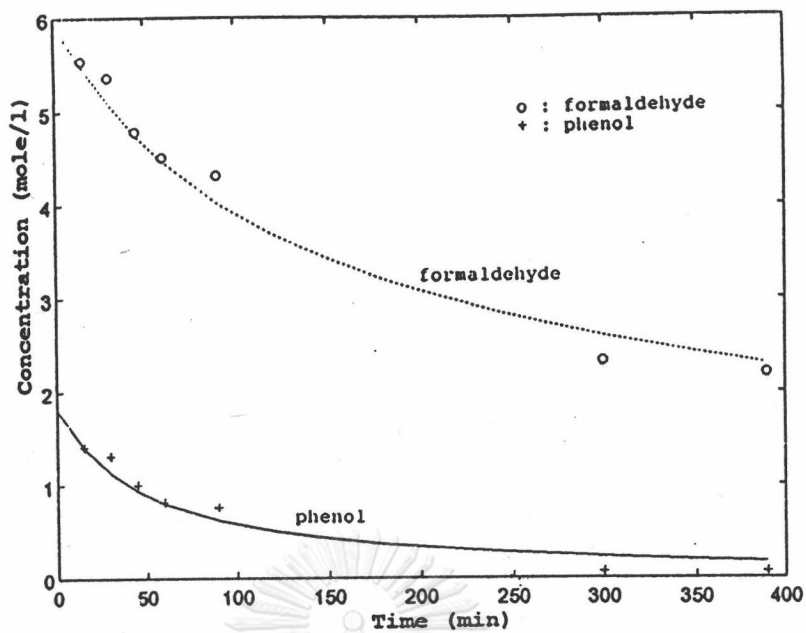


Figure 5-22 Reactant concentration vs. time at 30°C, $[P]_0=1.84$ M. $[F]_0 = 5.94$ M. $[\text{NaOH}]_0=1.84$ M.: Curve: calculated. Point: experimental data (Freeman et.al (1954)).

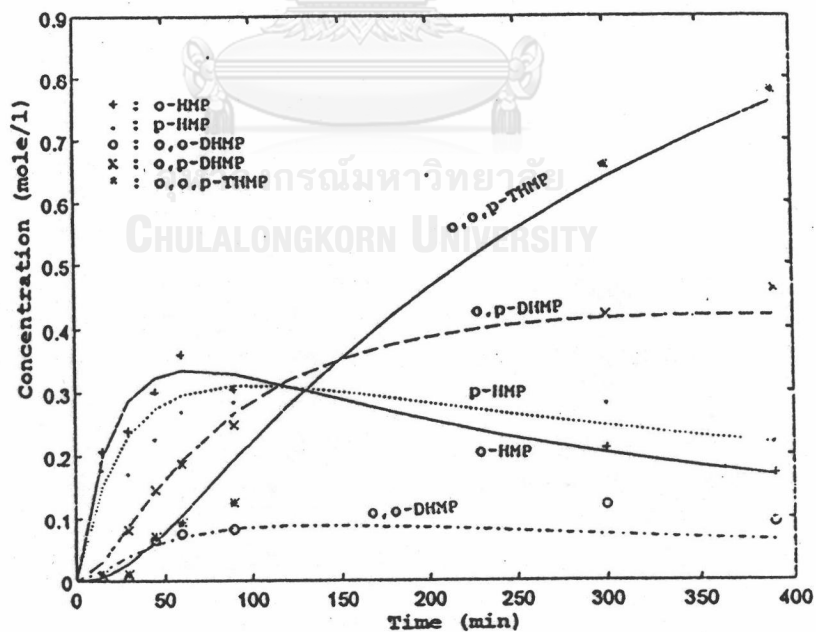


Figure 5-23 Product concentration vs. time at 30°C, $[P]_0=1.84$ M. $[F]_0 = 5.94$ M. $[\text{NaOH}]_0=1.84$ M.: Curve: calculated. Point: experimental data (Freeman et.al (1954)).

Figure 5-18 to 5-23 show the concentration profiles of each product species in the different conditions as described below the figures. The profiles in each Figure show the same manner. o-HMP concentrations are greater than p-HMP even though the reactivity of each site is smaller than p-HMP site because of two ortho sites on phenol molecules. Thus rate of o-HMP formation is greater than p-HMP formation.

o,o-DHMP concentrations are the lowest because rate of disappearance to form o,o,p-THMP are greater than rate of formation, $k_6 > k_3$.

o,p-DHMP accumulate and tend to higher as the reaction time proceed, because they are formed from both o-HMP and p-HMP in higher rate than rate of disappearance to form o,o,p-HMP.

o,o,p-THMP are accumulate and tend to higher because they are formed from both o,o-DHMP and o,p-DHMP but no disappearance.

Figure 5-24 shows the effect of temperature and base concentration on rate of reaction. Rate of reactions in higher temperature are higher than in the lower temperature. Base concentration in 50 °C are two times in 60 °C. The curves show almost the same rate.

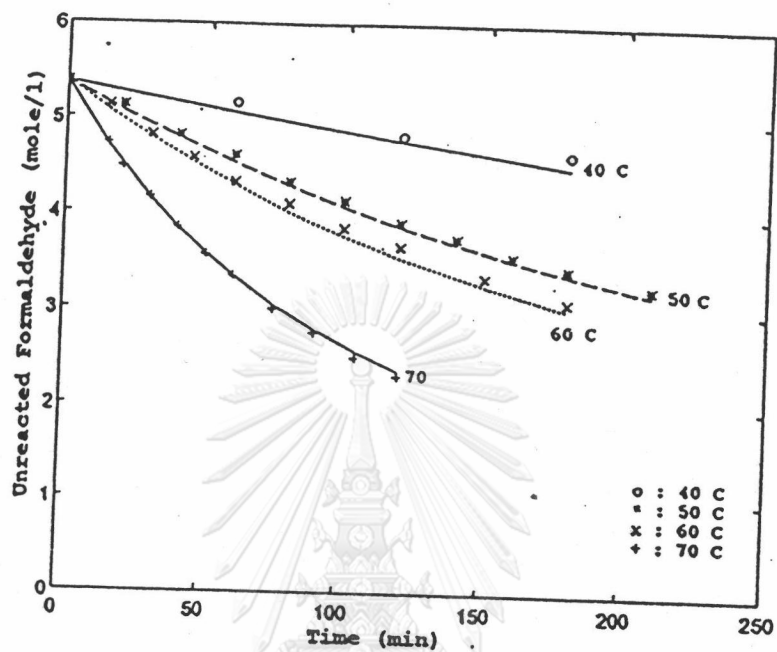


Figure 5-24 Formaldehyde concentration vs. time at various temperature. Curve: calculated.
 Point: experimental data (DeJong et.al (1952))
 $[P]_0 = 5.375$ M. $[F]_0 = 5.375$ M.
 Temp. = 40 °C : $[\text{NaOH}]_0 = 0.1$ M.
 Temp. = 50 °C : $[\text{NaOH}]_0 = 0.1$ M.
 Temp. = 60 °C : $[\text{NaOH}]_0 = 0.05$ M.
 Temp. = 70 °C : $[\text{NaOH}]_0 = 0.05$ M.

Figure 5-25 shows the effect of base concentration on rate of reaction. Rate of reaction in condition A is greater than the other condition, because of the highest concentration of NaOH. The more base, the more phenate ion formed. Rate of reaction in condition B, C and D are the same because of the equal concentration of NaOH.

Figure 5-26 shows overestimation in formaldehyde concentration between calculation and experimental data, because the initial concentrations of the reactants are so dilute that the calculated rate constants are less than the actual rate constant. Consequently, calculated rate of reaction was lower than the actual rate.

Figure 5-27 and 5-28 and table 5-7 and 5-8 show good agreement in formaldehyde concentration between calculation and experimental data.

Figure 5-29 shows the same result of the effect of NaOH concentration on rate of reaction as shown and discussed in Figure 5-25. The higher in NaOH concentration, the greater in rate of reaction.

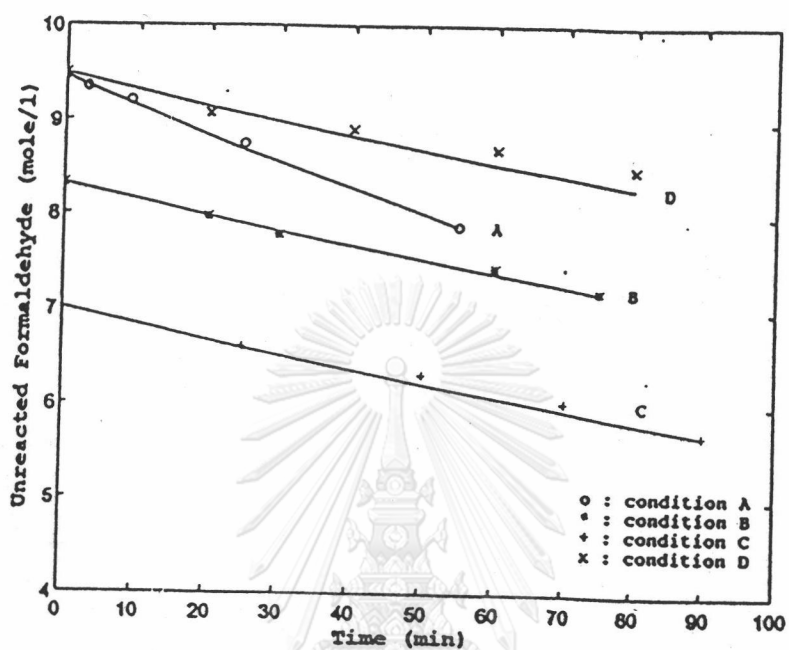


Figure 5-25 Formaldehyde concentration vs. time at various conditions. Temperature = 57 °C. Curve: calculated. Point: experimental data (Zavitsas et.al (1967))

A : $[P]_0 = 4.68 \text{ M}$. $[F]_0 = 9.46 \text{ M}$. $[\text{NaOH}]_0 = 0.0953 \text{ M}$.
 B : $[P]_0 = 4.80 \text{ M}$. $[F]_0 = 8.53 \text{ M}$. $[\text{NaOH}]_0 = 0.0462 \text{ M}$.
 C : $[P]_0 = 4.95 \text{ M}$. $[F]_0 = 7.01 \text{ M}$. $[\text{NaOH}]_0 = 0.0489 \text{ M}$.
 D : $[P]_0 = 2.85 \text{ M}$. $[F]_0 = 9.49 \text{ M}$. $[\text{NaOH}]_0 = 0.0449 \text{ M}$.

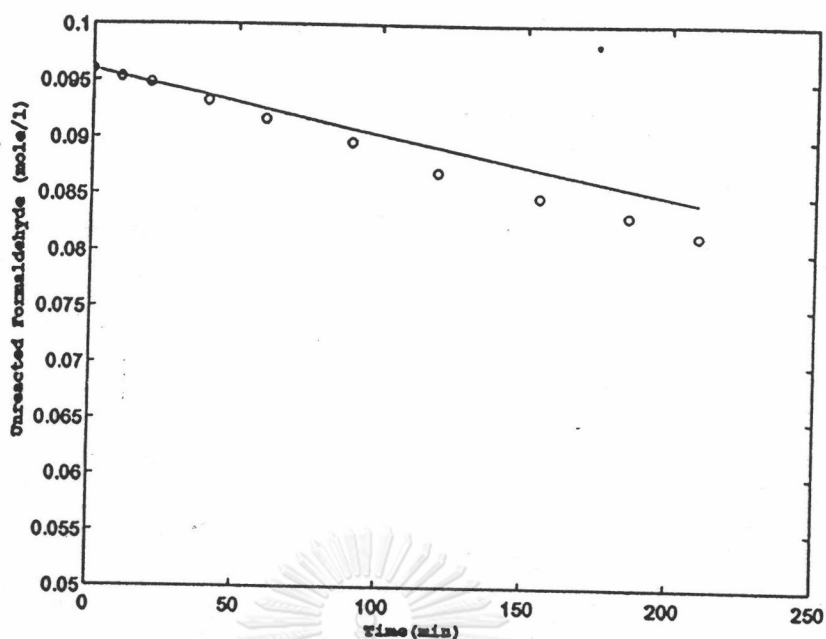


Figure 5-26 Formaldehyde concentration vs. time at 31 °C.
 $[P]_0 = 0.4$ M. $[F]_0 = 0.09602$ M. $[\text{NaOH}]_0 = 0.2$ M.
 Curve: calculated.
 Point: experimental data (Dijkstra et.al(1957)).

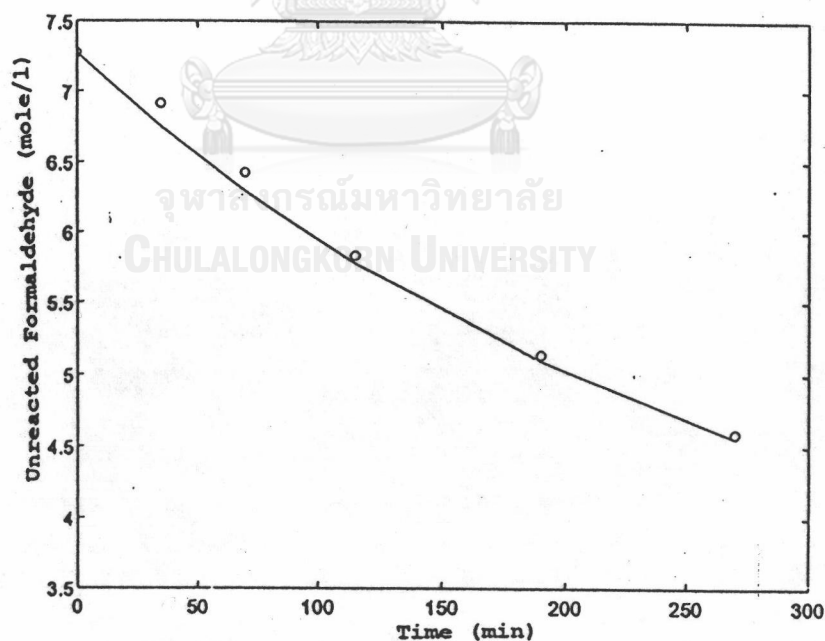


Figure 5-27 Formaldehyde concentration vs. time at 57 °C.
 $[P]_0 = 4.694$ M. $[F]_0 = 7.27$ M. $[\text{NaOH}]_0 = 0.04388$ M.
 Curve: calculated.
 Point: experimental data (Zavitsas et.al(1968)).

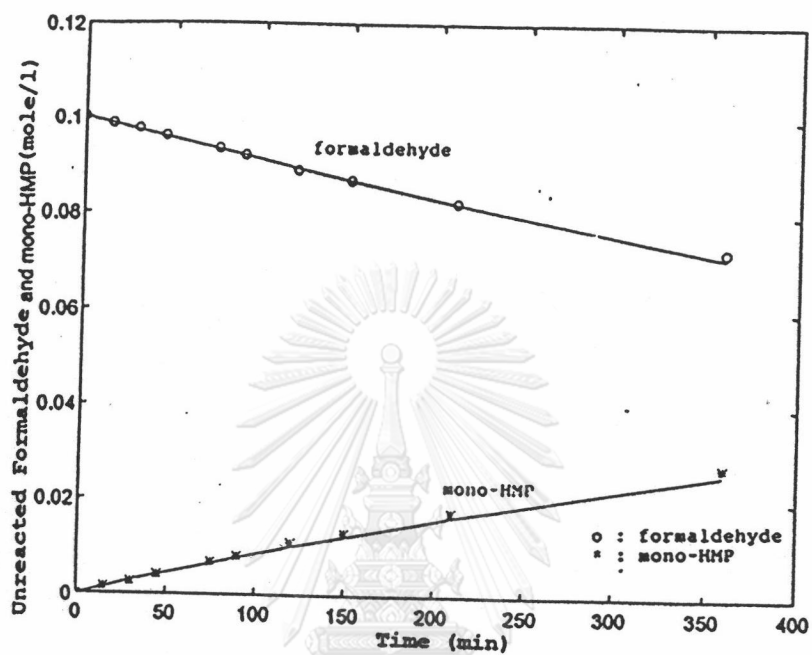


Figure 5-28 Formaldehyde and product concentration vs. time at 90°C. $[P]_0 = 0.2$ M. $[F]_0 = 0.05$ M. $[\text{NaOH}]_0 = 0.0045$ M. Curve: calculated. Point: experimental data (Dijkstra et.al(1957)).

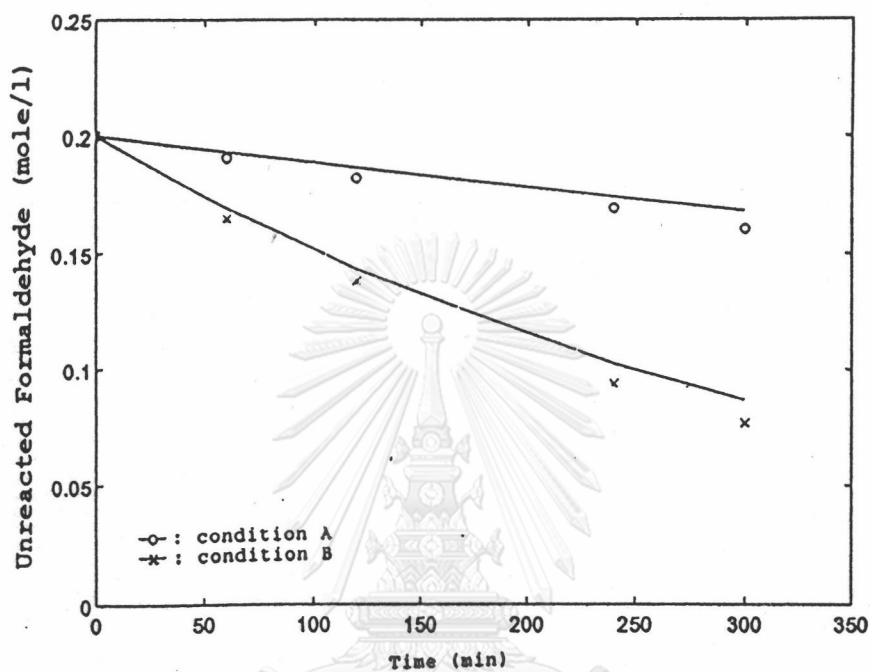


Figure 5-29 Formaldehyde concentration vs. time at 30 °C.
 $[P]_0 = 2.0 \text{ M}$. $[F]_0 = 0.2 \text{ M}$.
 Curve: calculated.
 Point: experimental data (Peer et.al(1959)).
 Condition A : $[\text{NaOH}]_0 = 0.13 \text{ M}$.
 Condition B : $[\text{NaOH}]_0 = 0.6 \text{ M}$.



Table 5-7 Simulation Results from Simulating Condition
of Case 20 (Zavitsas et.al(1968))

$[P]_0 = 4.42 \text{ M.}, [F]_0 = 9.3 \text{ M.}, [\text{NaOH}]_0 = 0.0937 \text{ M}$

Temperature = 45 °C

Reactant and Product	Concentration (mole/l)			
	Reaction time = 6 Hr		Reaction time =20 Hr	
	Experiment	Calculate	Experiment	Calculate
Phenol	2.632	2.597	1.332	1.33
Formaldehyde	6.944	6.931	4.187	4.28
o-HMP	0.775	0.832	0.919	0.96
p-HMP	0.525	0.531	0.70	0.69
o,o-HMP	0.13	0.127	0.294	0.27
o,p-HMP	0.237	0.243	0.66	0.67
o,o,p-HMP	0.075	0.087	0.53	0.50

Table 5-8 Simulation Results from Simulating Condition
of Case 12 (Zavitsas et.al(1968))

$[P]_0 = 4.77 \text{ M.}$, $[F]_0 = 8.47 \text{ M.}$,

$[\text{NaOH}]_0 = 0.2860 \text{ M.}$ Temperature = $30 \text{ }^\circ\text{C}$

Reactant	Concentration (mole/l)	
and	Reaction time = 28 Hr.	
Product	Experiment	Calculate
Phenol	1.863	1.88
Formaldehyde	4.04	4.06
o-HMP	0.97	0.98
p-HMP	0.72	0.75
o,o-HMP	0.27	0.22
o,p-HMP	0.59	0.58
o,o,p-HMP	0.38	0.36

The Proposed model has been applied to another system, MgO catalyzed system. Rate constants were estimated by comparing with experimental data of Zavitsas et.al(1968) at 57 °C. Figure 5-30 and 5-31 show the concentration profiles of reactants and products calculated with rate constants obtained ($k_1=0.135$, $k_2=0.025$, $k_3=0.1545$, $k_4 = 0.06$, $k_5=0.1$, $k_6=0.0565$, $k_7=0.0989$ in l/mole.min). The results show that in MgO catalyzed system, the o- sites are much more reactive than the p-site ($k_1 > k_2 = 5$). The concentrations of o-HMP, o,o-DHMP and o,o,p-THMP are high as the same results reported from Fraser et.al(1959) that the presence of bivalent metal ions such as Mn^{++} and Mg^{++} has been found to catalyse the production of o-HMP and o,o-DHMP.

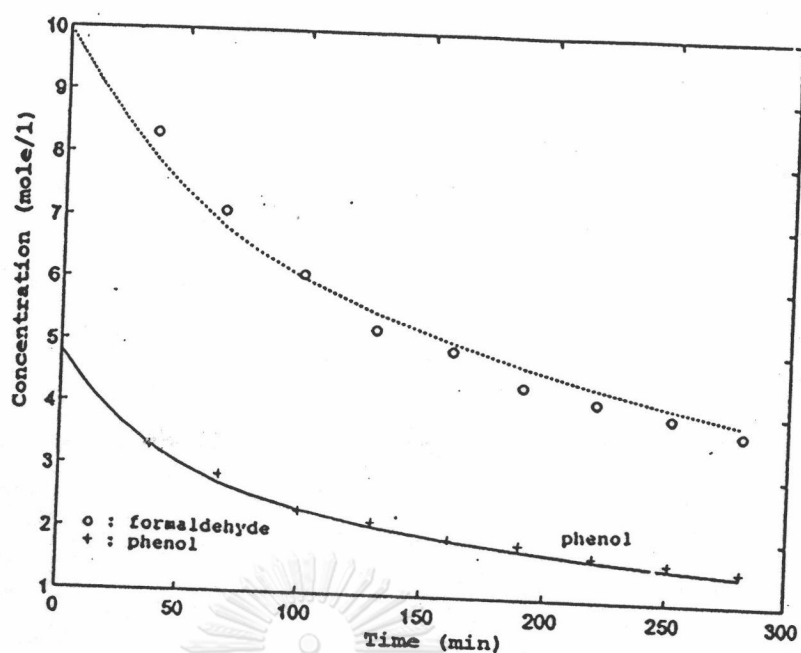


Figure 5-30 Reactant concentration vs. time at 57°C.
 $[P]_0 = 4.815 \text{ M}$. $[F]_0 = 9.963 \text{ M}$. $[\text{MgO}]_0 = 0.232 \text{ M}$.
 Curve: calculated.
 Point: experimental data (Zavitsas et.al(1968)).

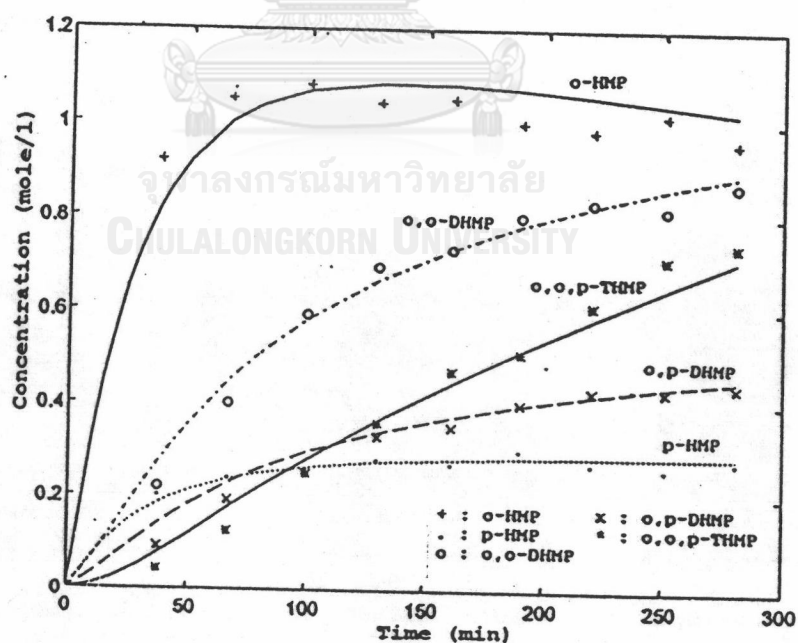


Figure 5-31 Product concentration vs. time at 57°C.
 $[P]_0 = 4.815 \text{ M}$. $[F]_0 = 9.963 \text{ M}$. $[\text{MgO}]_0 = 0.232 \text{ M}$.
 Curve: calculated.
 Point: experimental data (Zavitsas et.al(1968)).